

CCXXXI.—*The Essential Oil of Cocoa.*

By JAMES SCOTT BAINBRIDGE and SAMUEL HENRY DAVIES.

IN the older literature it is always assumed that the aromatic substance in cocoa is either identical with cocoa-red or associated with it. Cocoa-red, the colouring matter of fermented cocoa, was shown by Hilger and Lazarus (*Apoth. Zeit.*, 1892, 7, 469) and by Schweitzer (*Pharm. Zeit.*, 1898, 43, 389) to be obtained by splitting up the cocoa glucoside, which is stated to be resolved into one molecule of cocoa-red, six of dextrose, and one of theobromine. There is, however, nothing in the composition of cocoa-red to suggest an aromatic substance with a powerful flavour, and it is natural to assume that the distinctive flavour and aroma in this, as in all similar seeds, might be due to the presence of an essential oil. Again, cocoa-red, when prepared in a pure state, appears to be absolutely devoid of flavour. This was established beyond doubt by W. A. Caspari in this laboratory in 1901–2. Repeated attempts were then made to isolate an essential oil. It was found that the odour of cocoa clung with extraordinary persistence to the spirit used for extracting it. The spirit reacted decidedly with Schiff's reagent, but it was impossible to isolate the flavour by treatment with sodium hydrogen sulphite or phenylhydrazine. An aqueous distillate of the cocoa was also impregnated with cocoa flavour, but this was not persistent like the flavour in spirit. At that time, attempts to distil larger quantities of cocoa and to isolate the essential oil from the distillate with benzene were unsuccessful, the material isolated principally consisting of fatty acids.

In 1908 Dr. J. Sack, of the Government Agricultural Laboratory in Surinam, in the course of an article on the fermentation of cocoa (*Inspectie van den Landbouw in West Indie*, Bulletin 10, Jan., 1908) described the distillation of pulverised fermented cocoa with steam, whereby a small amount of an essential oil was obtained possessing the aroma and flavour peculiar to cocoa. Twenty kilograms of cocoa are said to have yielded 1 c.c. of oil, which, however, does not appear to have been further investigated.

We have subsequently carried out the distillation of large quantities of cocoa nibs, and have succeeded in obtaining sufficient of the essential oil for the investigation described in this communication. There can be no doubt that the material isolated was a true essential oil; it possessed an intense odour of cocoa, and the flavour was clearly perceptible in a dilution of 1 in 50 million parts of dilute syrup. The flavour is most nearly akin to that of coriander oil.

Before dealing in detail with the physical and chemical exam-

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ination of the oil, we may point out that the method of preparing cocoa beans in the tropics by fermentation and slow drying, adds to the number of possible ethereal substances present in the crude oil. To explain this, we must briefly refer to the method of fermentation practised in South America and the West Indies.

The cocoa-pods are cut open, the contents scooped out and conveyed into large tanks or boxes, where the sweet, viscous pulp, in which the beans are embedded, ferments and forms a thin alcoholic and acid liquor, which largely drains away.

The first runnings from a fermenting box in Jamaica, taken fifteen hours after the pods were broken, had the following composition :

Specific gravity, 1.023.

	Percentage by weight.
Total solids	5.75
Ash	0.51
Reducing sugars (as invert sugar) ...	3.5
Pectin	1.97
Alcohol	4.88
Total acidity (as acetic acid)	0.78
Volatile acid (, ,)	0.58
Nitrogen	0.05

The ash consists chiefly of sodium, potassium, and calcium carbonates and phosphates.

The non-volatile acid consists largely of tartaric; no succinic, citric, or malic acid could be detected. No sucrose is present.

Part of this liquor penetrates into the beans, which are thus saturated with the products of fermentation, but the shell membrane is fine enough to prevent the micro-organisms from percolating to the kernels.

The course of fermentation may be briefly described from unpublished observations made by one of us in the West Indies.

The beans and adherent pulp, which are commonly at a temperature of 26—28° when placed in the fermenting box, rapidly become warmer. During the first twenty-four hours the temperature rises to 35° or 40°, varying with the exact position in the box. Within forty-eight hours it rises to 40—45°, and if the fermentation is continued for five or six days the temperature will be found to rise to a maximum of 45—50°. Higher temperatures are occasionally noted, but they rarely exceed 53°. If the fermentation is continued for the exceptionally long period of ten to eleven days, as is the custom on certain Trinidad estates, the temperature will fall slightly towards the close. It is customary to transfer the contents of the fermenting boxes from one box to another every two or three days. Some form of false bottom is provided, and

the cover is loose, so that partial aeration goes on throughout the process. The quantity of cocoa dealt with in each box represents, on an average, the contents of 8000 to 16,000 pods, or 12—24 cwt. of wet material. The outside of the bean changes from white or pale pink to rich brown; characteristic odours are evolved, and a vigorous fermentation takes place. The stages of this fermentation may be distinguished thus:

First, a large growth of *Saccharomyces apiculatus*, together with small quantities of *Saccharomyces anomalus*, etc., doubtless derived from the surface of the pod husks. This stage lasts about twelve hours.

Secondly, as in spontaneous wine fermentation, an enormous development of true *Saccharomyces* occurs, exhibiting typical oval and round cells. If the temperature rises normally, no formation of new cells is noted after the first forty-eight hours. The alcohol produced soon arrests the growth of *Sacch. apiculatus* and the "wild" yeasts. A quantity of alcoholic liquor drains away.

The third stage of fermentation is characterised by a very large growth of acetic acid bacteria, a great number being carried to the fermenting boxes by swarms of the "vinegar fly" (*Drosophila*). The drainings now consist of a dilute vinegar. The complete mixing of the mass every second or third day ensures the presence of these organisms in every part of the fermenting mass. If the temperature does not rise above 50°, the acetic bacteria continue to grow during the remainder of the fermentation.

A fourth stage is reached if the fermentation is prolonged beyond eight days, when a growth of spore-bearing bacilli of the *Bacillus subtilis* type becomes evident.

In addition to these successive fermentations it will be found that when the cocoa is turned out from the fermenting boxes and dried slowly in the sun, as is often the case, a modified fermentation takes place at night, so long as the beans are sufficiently moist, and large colonies of wild yeast and bacteria become visible on the surface of the beans.

With the advance of fermentation the change of odour is marked; the sweet, fruity, and alcoholic odour of the early stage changes to a strongly alcoholic, and this to an ethereal odour suggesting ethyl acetate. Later a strong acetic acid odour supervenes, but this is always accompanied by fruity and ethereal components. Finally, if the fermentation is prolonged and putrefactive organisms predominate, an odour resembling that of high game is evolved.

It is obvious that a number of the products resulting from these complex fermentations will percolate into the bean, and of these the less volatile constituents will remain in the dry kernel. Conse-

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quently we shall expect to find that the true essential oil of cocoa is accompanied by a certain number of esters and higher alcohols, analogous to those produced in other spontaneous fruit fermentations taking place at comparatively high temperatures in presence of a free supply of air.

Isolation of Essential Oil.

Our first experiments were carried out with fermented Trinidad cocoa beans of good quality. A preliminary experiment was made with raw, and a second with roasted beans, using quantities of 150 kilos. The amount of crude oil obtained from 150 kilos. of cocoa was 4 to 5 c.c., obviously insufficient for fractional distillation. After successive trials with 250 and with 1000 kilos., we finally subjected 2000 kilos. of cocoa to distillation in 100 kilo. lots.

The cocoa employed in the final experiment is known in commerce as "Arriba"; it represents the best fermented product of Ecuador. It was chosen on account of its strong aromatic and spicy flavour, suggesting an exceptionally large content of essential oil. The beans were lightly roasted, the shell removed by the ordinary nibbing process, and the warm nibs, without being ground, were subjected to pressure in hydraulic presses to remove as much cocoa-butter as possible. The cake was carefully broken up to avoid reducing it to a fine powder, so that it presented a porous substance through which steam could readily percolate.

The crushed nibs were then submitted to a steam distillation, using clean steam, superheated to an average temperature of 120°. For each charge of 100 kilos. about 40 litres of water were condensed at the rate of 20 litres per hour; this was immediately shaken with specially purified light petroleum (b. p. 25—38°), and the shaking out repeated a second time. The petroleum extracts were collected and concentrated (at 25—27°/500—550 mm.) from a volume of 55 litres to 3½ litres. This was dried over calcium chloride, concentrated to half a litre, washed repeatedly with *N*/2-potassium hydroxide, then with water, and several times with *N*/2-sulphuric acid, finally removing every trace of acid by washing with water. The residual light petroleum was then removed in a vacuum. In this way 24 grams of oil were obtained from 2000 kilos. of cocoa, a quantity not exceeding 1 part in 100,000 of the original cocoa beans.

The oil obtained from the preliminary experiment had a specific gravity of 0.9075 at 15° and refractive index of 1.4728 at 20°. It contained no sulphur, and gave the following numbers on analysis: C=75.57; H=10.45; N=1.3. The oil was subjected to repeated fractional distillation in a vacuum.

Trustworthiness of Method of Distillation.

In order to determine whether all the essential oil had been separated under the conditions of our distillation, we submitted a batch of cocoa, already exhausted with steam in the usual way, to a rapid treatment with superheated steam. Ninety per cent. of the distillate proved to be free fatty acid, and the unsaponifiable oil, which had a marked lemon-grass odour, represented only 0.09 gram per 1000 kilos. of cocoa; a negligible quantity.

We also treated an exhausted batch of cocoa with 1 per cent. of its weight of sulphuric acid, and then submitted it to a rapid treatment with highly superheated steam (128°) with the view of hydrolysing any ester of high boiling point which might not have volatilised in the first steam distillation.

From 75 kilos. of cocoa, 0.408 gram of a pale yellow oil was obtained, which had a very penetrating odour suggesting valeric acid and cocoa. It was found to consist of: (a) a non-acidic substance, presumably cocoa oil, weighing only 0.027 gram, a quantity too small for investigation, and (b) an acid which proved to be hexoic. (Found, C=62.0; H=10.0. $C_6H_{12}O_2$ requires C=62.03; H=10.34 per cent.) As hexoic acid is known to be formed when cocoa-butter is distilled with steam, we may conclude that our method of distillation removes practically the whole of the essential oil.

In the aqueous distillate, after extraction with light petroleum, the presence of ethyl alcohol, acetic, propionic and butyric acid was proved. These are undoubtedly the products of the fermentation of the cocoa bean.

Alkaline Solution.

The oil in solution in light petroleum was washed four times with 25 c.c. of *N*/2-potassium hydroxide in an atmosphere of nitrogen, light being excluded. The alkaline solution was saturated with carbon dioxide and extracted with light petroleum, from which 0.201 gram of octoic acid was obtained. (Found, C=66.64; H=11.27. $C_8H_{16}O_2$ requires C=66.66; H=11.11 per cent.) The alkaline solution was acidified and distilled in a current of steam, and the residue extracted with light petroleum, from which valeric acid was obtained. (Found, C=60.48; H=9.59. $C_5H_{10}O_2$ requires C=58.83; H=9.8 per cent.) The steam distillate had an odour of butyric acid; it yielded an acid, which by analysis of the silver salt proved to be a mixture of octoic and *n*-nonoic acids.

We conclude that the free acids in cocoa-oil consist of valeric, octoic, *n*-nonoic, and possibly hexoic acids.

Acid Solution.

The oil solution was then washed with $N/2$ -sulphuric acid, from which 0.085 gram of a yellow oil with a disagreeable, pungent odour was obtained. It contained 10 per cent. of nitrogen, but was not further examined.

Absence of Primary Alcohols.

All the light petroleum extracts of cocoa-oil were dried over calcium chloride, which was then dissolved in much water, and distilled in a current of steam. No alcohol could be detected in the distillate, and this was taken as evidence that no primary alcohol was present in the oil.

Fractional Distillation of Purified Oil.

The light petroleum solution of the purified oil was distilled in a small Claisen flask. When practically all the petroleum had been removed, the flask was connected to a Brühl receiver, the whole placed under a vacuum, and the remaining air displaced by nitrogen. The oil was then distilled and twice redistilled, and the final fractions were kept in the dark in closed tubes filled with nitrogen.

The residues from the first and second fractional distillations were subjected to a very high temperature to separate any esters of high boiling point such as benzyl benzoate, but even at $205^{\circ}/7.5$ mm. no distillate could be recovered, whilst the residue was frothing and evidently decomposing. The portion of the residue soluble in alcohol was extracted with light petroleum, and washed with sodium carbonate to remove the acid. The acid, the silver salt of which was moderately soluble in water, was extracted and purified by conversion into the sodium salt, and proved to be octoic acid. (Found, C=68.17; H=10.92. $C_8H_{16}O_2$ requires C=66.66; H=11.11 per cent.)

The non-acidic substances were probably oxygenated decomposition products.

Fraction (1), which weighed 0.51 gram, and boiled at $49-53^{\circ}/21$ mm., with a refractive index of 1.4299, had a pleasant ethereal odour suggestive of certain amyl esters:

0.1799 gave 0.4276 CO_2 and 0.1617 H_2O . C=64.8; H=10.0 per cent.

The analytical numbers are, by a coincidence, near those required by amyl acetate (C=64.61; H=10.77 per cent.), but on saponification, 0.231 gram required 9.54 c.c. $N/10$ -potassium hydroxide, giving

an ester number of 231; this corresponds with only 53.6 per cent. of amyl acetate. The products of saponification proved to be: (a) acetic acid, and (b) a mixture of amyl alcohol, and an unsaponifiable oil with a lemon-grass odour.

Fraction (2), which weighed 1.51 grams, and boiled at 57—70°/19.5—15.5 mm., with a refractive index of 1.4529, had an odour resembling that of the previous fraction, but with a stronger infusion of the lemon-grass substance:

0.2052 gave 0.4891 CO₂ and 0.1715 H₂O. C=65.0; H=9.29 per cent.,

a result resembling fraction (1).

On saponification an ester number of 150 (corresponding with 39 per cent. of amyl acetate) and acid number of 26.5 were recorded. The products of saponification were: (a) an insoluble acid, which proved to be octoic, (b) a soluble acid consisting of a mixture of acetic and propionic acids, and (c) an alcohol which could not be completely separated from the accompanying unsaponifiable oil; its boiling point (130—138°) and characteristic odour agreed with amyl alcohol.

Fraction (3), which weighed 0.6 gram, boiled at 70—84°/15 mm., and had a refractive index of 1.4688. This is an intermediate fraction, still containing a considerable proportion of the fermentation esters, but a larger proportion of the main constituents of the oil. The acid number was 37.6, and the ester number, 93.7, was equivalent to 22 per cent. of amyl butyrate. The products of saponification include (a) an insoluble acid, the barium salt of which gave an analysis approximating to *n*-nonoic acid, (b) a soluble acid, in too small quantity for analysis, yielding an ethyl ester with a marked odour of ethyl butyrate, and (c) unsaponifiable, consisting of a small quantity of a yellow oil with a mixed "amyl" and cocoa odour.

0.294 Gram was acetylated, and 0.138 of the resulting oil required 5.3 c.c. *N*/10-potassium hydroxide to saponify it, yielding an acetylation number of 215.2, which with an ester number of 93.7 gave an alcohol number of 121.5. This is equivalent to 33 per cent. alcohol, C₁₀H₁₈O, in the original oil (see fraction 5).

Oxidation Products.—The unsaponifiable matter and alcohol were extracted, mixed with the similar products of saponification of the oil [(c) above], and oxidised with potassium dichromate and sulphuric acid in excess. The liquor, after being rendered alkaline, was freed from the remaining oil and distilled. The distillate was found to contain acetone (*p*-bromophenylhydrazone, m. p. 89—91°). The residue was acidified, and the insoluble acid extracted with ether. This consisted of 0.028 gram of white crystals mixed with

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some oil, and the analysis of the barium salt indicated a mixture of octoic and lævulic acids.

A further oxidation of the neutral product gave a minute quantity of white solid, melting below blood-heat, probably consisting of impure lævulic acid (m. p. 33°). The soluble volatile acid was distilled off, and the analysis of the barium salt indicated that it was a mixture of acetic and propionic acids. (Found, Ba=50.0. Calc., Ba=53.7 and 48.4 per cent. respectively.)

We conclude that the products of oxidation are acetone, acetic and propionic acids, lævulic and *n*-nonoic acids.

Fraction (4), which weighed 9.7 grams, boiled at $87-97^{\circ}/11-15$ mm., and had a freezing point below -16° ; its refractive index was 1.4658_{20} , specific gravity 0.8936 $15^{\circ}/15^{\circ}$, and the specific rotation $[\alpha]_D^{20} + 11^{\circ}36'$. A qualitative test showed the absence of sulphur.

This was the middle and most important fraction, and constitutes with (5) the bulk of the oil. Its odour, whilst resembling that of cocoa, was also reminiscent of coriander and lemon-grass:

0.2284 gave 0.6335 CO_2 and 0.2233 H_2O . C=75.63; H=10.86.

0.2534 ,, 0.7020 CO_2 ,, 0.2485 H_2O . C=75.56; H=10.90.

0.20 ,, 0.9 N_2 at 21° and 766 mm. N=0.52.

The molecular weight was determined by the cryoscopic method with benzene as solvent.

It was found that the molecular weight increased with concentration, which suggests association of the solute; to obtain a true result, very dilute solutions were used:

0.0382 in 9 of benzene gave $\Delta t = -0.148$. M.W.=143.

0.0786 ,, 9 ,, ,, $\Delta t = -0.291$. M.W.=150.

0.1195 ,, 9 ,, ,, $\Delta t = -0.439$. M.W.=151.

The true molecular weight may be taken to be about 150. The property of association in solution points to the probable presence of tertiary alcohols.

No ketone or aldehyde was present, and the oil was not changed by treatment with sodium amalgam for twenty-four hours.

Oxidation by permanganate in acid solution gave acetone and propionic acid, and by ammoniacal silver oxide, valeric acid.

2.003 Grams of oil were acetylated, and 0.514 of the resulting oil required 3.1 c.c. of *N*/2-potassium hydroxide to saponify it. This gave an acetylation number of 170.8, which with an ester number of 33 (see below) gave an alcohol number of 137.8, which is equivalent to 42 per cent. of an alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$ (see fraction 5), in the original fraction.

2.04 Grams of oil required 1.0 c.c. *N*/2-potassium hydroxide to

neutralise, giving an acid number of 13·7, and 2·4 c.c. *N*/2-potassium hydroxide to saponify, giving an ester number of 33.

The products of saponification include: (a) an insoluble acid, which on analysis of the barium salt proved to be octoic acid; (b) a soluble acid, which proved to be butyric acid; and (c) a neutral constituent, which resembled the original fraction in odour and elementary composition. This formed the bulk of the oil, and indicated that the main constituent is unaffected by saponification. It was then oxidised with potassium dichromate and sulphuric acid, and the products were found to include acetone (*p*-bromophenylhydrazone, m. p. 90—92°), propionic, *n*-nonoic, and valeric acids, together with 0·6 gram of a yellow oil, which had an odour suggesting impure citral or methylheptenone. A very small quantity of an impure semicarbazone was prepared, but this only served to prove the presence of an aldehyde or ketone. By means of the bisulphite compound, a minute quantity of methylheptenone was obtained, but the main constituent passed into solution, probably as the disulphonate of citral; this was later proved to be the case by an approximate analysis of the compound. The small quantities dealt with make identification extremely difficult, but we believe the products of oxidation to be citral and possibly methylheptenone, acetone, propionic, *n*-nonoic, and valeric acid.

The results of bromination will be found under fraction (5).

Fraction (5), which weighed 3·1 grams, and boiled at 97—99°/10 mm. (b. p.=210°/760 mm.), had a refractive index of 1·4660. In odour it resembled fraction (4); it was somewhat greener when fresh, but darkened on keeping:

0·2081 gave 0·5608 CO₂ and 0·2003 H₂O. C=73·49; H=10·67 per cent.

On saponification, 0·494 gram required 0·2 c.c. *N*/2-potassium hydroxide to neutralise, giving an acid number of 11·0, and 0·5 c.c. *N*/2-potassium hydroxide to saponify, giving an ester number of 28·6. The products of saponification were found to consist of hexoic and propionic acids, together with unsaponifiable matter which was submitted to oxidation (see below).

A portion of the oil was acetylated, and 0·476 gram of esterified oil required 3·5 c.c. *N*/2-potassium hydroxide to saponify, giving an acetylation number of 207·8, which, with an ester number of 28·6, gave an alcohol number of 179·2. This corresponds with 57 per cent. of linalool (see below) in original fraction. Experiments with pure linalool show that it is not readily acetylated, and that only 80 per cent. of it forms an ester under the conditions of the experiment. This agrees with observations made by Gildemeister and by Parry. It is therefore necessary to add 25 per cent. to the

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quantity of linalool determined by acetylation, to get an approximate idea of the amount actually present. This would give 71 per cent. of linalool in fraction (5).

The neutral product of the saponification was oxidised with potassium dichromate and sulphuric acid, using the equivalent of one atom of oxygen per molecule of alcohol. The oxidation proved to be incomplete, and butyric acid alone was identified amongst the products.

A phenylurethane derivative of the alcohol was prepared, using 0.5 gram of oil. After purification, the compound was found to consist of white crystals melting at 55—59° (linaloolphenylurethane melts at 64—66°). (Found, C=76.0; H=8.7; N=5.8. Linaloolphenylurethane requires C=74.7; H=8.44; N=5.1 per cent.) The experiment was repeated with double the quantity of oil, and white needles separated, which melted at 60—61°, but the bulk of the material was very impure and contained N=6.4 per cent. Although the above agreement is poor, we may conclude that linalool is the main alcohol of fraction (5), and doubtless also of fraction (4). This is confirmed by comparing the physical constants of fraction (4) with *d*-linalool:

		<i>d</i> -Linalool, C ₁₀ H ₁₈ O.	Cocoa oil, fraction (4).
Gildermeister *	b. p. at 760 mm.	198—199°	195—210° (calc.)
	13 "	88.3—89.5°	87—97 (15—11 mm.)
	D ₁₅	0.870	0.8936
	n _D ²⁰	1.4668	1.4658
Schmidt †	[α] _D ²⁰	+13°19'	+11°36'
(for coriandrol)	M. W.	154	150 (approx.)

* *Arch. Pharm.*, 1895, **233**, 179.

† *Ber.*, 1898, **31**, 834.

As a further proof of the presence of linalool it was proposed to acetylate the alcohol and separate the resulting geranyl acetate from the other constituents by distillation. The esterification was carried out in the usual way on 1.0 gram of oil, and the product fractionally distilled under diminished pressure. The middle fraction, boiling at 100—104°/4—2.5 mm. (b. p. 240°/760 mm. approx.), had an odour resembling that of geranyl acetate. (Found, C=70.23; H=9.44. C₁₂H₂₀O₂ requires C=73.47; H=10.2 per cent.) On saponification, 0.11 gram required 0.85 c.c. *N*/2-potassium hydroxide, giving an ester number of 235, corresponding with only 82 per cent. of geranyl acetate. This accounts for the poor agreement of the combustion figures.

The degree of unsaturation was determined by the bromine absorption in carbon tetrachloride solution; a parallel experiment was carried out on pure linalool. Cocoa-oil required per gram for substitution 1.092 grams, and for saturation 1.092 grams of

bromine, whilst linalool required 0.752 gram and 1.673 grams respectively. This determination is far from exact, but allowing for the fact that the oil is estimated to contain 71 per cent. of an alcohol, it is sufficient to prove that this alcohol has two double bonds.

Although the small quantities dealt with prevent exact individual determinations, the cumulative evidence of the presence of linalool is conclusive.

Thus cocoa-oil must be added to the considerable number of essential oils containing linalool, of which coriander, bergamot, neroli, ylang ylang, and linaloe are amongst the best known.

Fraction (6), which weighed 1.35 grams and boiled at 100—109°/10 mm., had a refractive index of 1.4707. It was darker in colour, and had a somewhat harsher odour than (4) and (5), which suggested the beginnings of decomposition:

0.246 gram gave 2.2 c.c. N_2 at 24° and 762 mm. $N=1.01$ per cent.

On saponification, 0.467 gram required 3.0 c.c. of 0.742 $N/10$ -potassium hydroxide to neutralise, giving an acid number of 26, and 5.6 c.c. of 0.947 $N/10$ -potassium hydroxide to saponify, giving an ester number of 62. This is double the ester number of fraction (5); the increase might be due to the presence of linaloyl acetate. 0.629 Gram was acetylated, and 0.5 gram of the esterified oil required 16.3 c.c. of 0.947 $N/10$ -potassium hydroxide to saponify, giving an acetylation number of 172.8, which, with an ester number of 62, gave an alcohol number of 110.8. This is equivalent to 30.5 per cent. of linalool in the original fraction. Among the products of saponification, impure octoic acid was identified. The unsaponifiable was expected to consist chiefly of linalool (or geraniol). 0.577 Gram was oxidised with potassium dichromate and sulphuric acid, and 0.211 gram of an oil was obtained, which had a pleasant odour of thyme, closely resembling that of methylheptenone. From this a semicarbazone was prepared, which, on purification, melted at 132—134°. Methylheptenonesemicarbazone melts at 136—137°. We may conclude that methylheptenone is an oxidation product; acetone was also identified, both being derived from linalool.

Fraction (7), which weighed 0.67 gram, and boiled at 109—116°/9—7.5 mm., had a refractive index of 1.4861. It was obviously decomposed, the odour being very flat and harsh. A series of unsuccessful experiments was made on this and other fractions to elucidate the composition of the nitrogenous substance.

Nitrogenous Constituent of Oil.

In preliminary experiments, repeated washing with acid and alkali failed to remove the nitrogenous substance. An attempt was made to free fraction (3), which contained N=0.94 per cent: (a) by boiling for two hours with 20 per cent. sodium hydroxide, but this only reduced the nitrogen to 0.65 per cent.; (b) by boiling for half an hour with 50 per cent. sulphuric acid; but this had still less effect, reducing the nitrogen to 0.73 per cent.

The purer oil of the final experiment contained less nitrogen, the two lower-boiling fractions of the final distillation none at all, the largest fraction (4) 0.52 per cent., fraction (6) 1.01 per cent., and the residue 1.8 per cent. Fraction (7), treated with stannous chloride and hydrochloric acid for an hour, gave a small quantity of amine, but the resulting material still contained N=3.4 per cent. Again, the residue from the second fractionation, after boiling with concentrated hydrochloric acid for six hours, still retained N=1.1 per cent. We conclude that there might be a small proportion of a nitro-compound present, but we were unable to throw any light on the composition of the main nitrogenous constituent.

Summary.

- (1) The aromatic principle of the cocoa bean is an essential oil.
- (2) Two thousand kilos. of cocoa nibs (deprived of some cocoa-butter) gave a yield of 24 c.c. of purified oil with a very powerful aroma and flavour of cocoa.
- (3) The oil was fractionally distilled three times, and the third distillation yielded seven fractions.
- (4) The early fractions were rich in esters, derived in all probability from the fermentation of the cocoa bean.
- (5) The middle fractions were rich in *d*-linalool, corresponding closely with coriandrol.
- (6) The amount of esters and of linalool may be estimated from the following table. Twenty-five per cent. of the amount of linalool determined by acetylation has been added in each case. The total linalool represents more than 50 per cent. of the cocoa oil.

Fractions.	Approx. calc. b. p./760 mm.	Weight in grams.	Percentage of esters.	Percentage of <i>d</i> -linalcol.
1	140°	0.51	54 as amyl acetate	Not determined
2	165	1.51	39 as amyl propionate	25
3	175—190°	0.6	22 as amyl butyrate	41
4	195—210	9.7	10 as hexyl (?) butyrate ...	53
5	210°	3.1	7 as hexyl (?) propionate...	71
6	220—230	1.35	22 as linaloyl acetate (?) ...	38
7	230—240	0.67	Not determined	Not determined

(7) In addition to the esters and linalool, from 4 to 10 per cent. of octoic acid (with hexoic and *n*-nonoic) was found in the different fractions.

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