THE OCCURRENCE OF FURAN DERIVATIVES IN VOLATILE OILS.

By B. Sanjiva Rao and K. S. Subramanian,
Department of Organic Chemistry, Indian Institute of Science, Bangalore.

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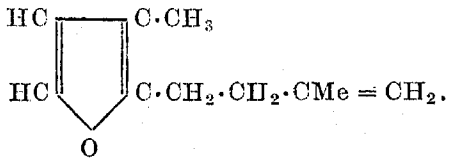
The most important of this group of compounds and also the first to be discovered is furfural, which was made by Dobereiner (*Ann.*, 1832, **3**, 141) by the action of sulphuric acid and manganese dioxide on sugar. It has been detected in minute quantities in the distillation waters of a number of volatile oils. The α-methyl- and dimethyl-furfural, also furfuralcohol have been known to occur in oil of cloves (Masson, *Compt. rend.*, 1909, **630**, 795), wood tar and roasted coffee beans. Furan, the parent compound of this group, has also been reported in Finnish turpentine (Atterburg, *Ber.*, 1880, **13**, 879). Kondo and Yamaguchi (*J. Pharm. Soc. Japan*, 1919, **446**, 263) isolated a small quantity of a compound $C_{10}H_{14}O$ from the oil of Perilla citriodora which has been reported to be



Some compounds belonging to the coumarone group of naturally occurring bodies in which the nucleus of furan is condensed with that of benzene and showing a lactonic behaviour as bergaptene have also been detected in volatile oils. These products occur, however, in small quantities. The presence of furan derivatives in volatile oils in quantity, has been considered rare and almost unknown (Finnemore, *The Essential Oils*, 1926, pp. 813, 860). There are, however, a few important instances of their occurrence in appreciable quantities, (*a*) benzyl-2-furylacetylene (Gilman, *J. Am. Chem. Soc.*, 1933, **55**, 3461) in *Carlina acaulis* (Semmler, *Ber.*, 1906, **39**, 726); (*b*) β-methylfuryl-isobutyl-ketone present in *Elsholtzia cristata*, Willd (Asahina and Murayama, *Arch. der. Pharm.*, 1914, **252**, 435); (*c*) the ketone ngaione from *Myoporum lœtum*, Forst. whose structure has not been definitely established (McDowell, *Perf. Ess. Oil Rec.*, 1921, **19**, 221). An examination of the oil from the leaves of *Clausena willdenovii*, W. and A. examined by the authors has shown that it consists almost exclusively of bodies containing the furan nucleus. The origin of these substances is not difficult to seek as

furfural is formed by the action of dilute acids on pentoses and pentosans present in nearly all naturally occurring cellulosic materials.

The oil from the same leaves grown in French India has been examined previously (*Report of Roure-Bertrand Fils*, April 1903, 35) and is stated to contain 11 per cent. ester (as $C_{10}H_{17}OCOMe$) and 6·2 per cent. alcohol ($C_{10}H_{18}O$). The essential oil obtained by the authors from the leaves was of a yellow colour and an agreeably weak fruity odour. It rapidly absorbed oxygen and was converted into a plastic resinous mass, and required to be freshly purified by distillation, prior to every experiment. The following percentages of the main constituents have been found to be present in the oil: oxides, α-clausenan ($C_{10}H_{12}O$; 58·0); di-α-clausenan ($C_{20}H_{24}O_2$; 23·0); β-clausenan ($C_{10}H_{14}O$; 6·0); ketones as $C_{10}H_{16}O$ (1·0); esters as furfuryl-geranate $C_9H_{15}COOC_5H_5O$ (4·0). The three oxides which are the main constituents are new substances and appear to belong to the furan group. An account of further experiments carried out with these oxides will be dealt with in the next communication.

The oil boils between 177–350° at atmospheric pressure. It was devoid of alcohols or phenols but gave an acetyl value. The lowest boiling oxide, β-clausenan is optically active unlike α-clausenan and di-α-clausenan which are both inactive. In β-clausenan purified through the ferrocyanic acid addition compound no hydroxyl group was found, but it gave an acetyl derivative on boiling with acetic anhydride. Either the oxygen ring has split, acetic acid adding on or acetylation has taken place after hydration of one of the double bonds in the side chain; the latter seems more probable as the acetyl derivative as well as the corresponding alcohol give the characteristic green and purple coloration with bromine like β-clausenan. On adding N/2 alcoholic potash to the acetyl derivative, some solid separated which being very minute was not further examined.

α-Clausenan whose molecular formula has been found to be $C_{10}H_{12}O$ is a clear colourless liquid having a pleasant lemony odour, distilling unchanged over sodium. It is the main constituent forming nearly 60 per cent. of the oil. It forms addition compounds with ferrocyanic and ferricyanic acids having the composition $2C_{10}H_{12}O.H_4Fe(CN)_6$ and $2C_{10}H_{12}O.H_3Fe(CN)_6$; either of the compounds can be used to separate or estimate the α-clausenan in a mixture. In this oil, both α- and β-clausenan can be estimated by this method. It was found that these acids had no other chemical action on α-clausenan. The molecular refraction of α-clausenan was found to be 45·74 while the calculated value assuming the presence of four double bonds and of a furan oxygen (atomic refraction constant, 1·2; *Ber.*, 1920, **53**, 1660) was 45·51. The parachor at 30°C. was found to be 381·1

and at 50°, 386·8 in agreement with the calculated value of 386·8. Associated liquids are known to show abnormal surface tension and low values for parachor. The observed value increases with temperature showing that α-clausenan is an associated liquid, which is supported by the higher molecular weight found by the freezing point method. The small degree of association found in the latter case may correspond to a high degree of association in the pure liquid.

α-Clausenan rapidly absorbs oxygen and is converted into a non-distillable resinous product on exposure to air or oxygen. The pure oxide keeps well in the absence of oxygen, and is soluble in all the organic solvents. It distils undecomposed at atmospheric pressure in a current of nitrogen or carbon dioxide but is slightly oxidised in air or oxygen. On boiling with water at atmospheric pressure or in a sealed tube at 170° from 2 to 6 hours it was quite uneffected except for slight oxidation and there was no indication of the oxide ring being split. It was unattacked by boiling acetic anhydride or alkalis, or keeping stirred with arsenic acid for twenty-four hours at ordinary temperature. Though the presence of four double bonds was indicated, it was recovered unchanged on treatment with sodium and alcohol. It gives a characteristic colour reaction with bromine in acetic acid and chloroform and also Liebermann's coloration. In acetic acid solution, a transient purple coloration is formed leaving the solution light blue; on further addition of bromine solution, it becomes deeper purple, blue and finally deep green. In chloroform solution, the transient purple coloration is formed leaving the solution green which becomes blue, purple and finally deep green with more bromine solution. No well-defined products could be separated by the action of bromine.

The constituent next in importance to α-clausenan, was a third oxide having the composition $C_{20}H_{24}O_2$; called di-α-clausenan, as it has double the molecular weight of α-clausenan. Though it is also an oxide, it does not form a sparingly soluble addition compound with ferrocyanic or ferricyanic acids unlike the other oxides occurring with it. It is a pale yellow liquid, very viscous unlike the others, and distils unchanged over sodium at a temperature of about 150° above the other two oxides. It is more rapidly oxidised than them in air or oxygen, but can be distilled at atmospheric pressure in a current of nitrogen. With bromine in acetic acid, it gives a transient rose red coloration leaving the liquid greenish yellow, becoming brown, red and finally brown with more bromine. It is soluble in most organic solvents except alcohol. The dilute mineral acids and glacial acetic acid give no coloration, while the concentrated acids are coloured red. It is unattacked by boiling acetic anhydride. The molecular refraction was

found to be 89·58 while the calculated value with seven double bonds and two furan oxygen atoms was 89·30. The parachor of this substance, 704 at 30° and 716·7 at 50°, is not in agreement with the calculated value 755·6. It appears more associated than α-clausenan.

Fractions 19-22, table II, which had an agreeable odour were found to consist mainly of ketones and esters. The acids obtained from the esters were separated into volatile and non-volatile portions. The former was found to be an unsaturated non-fatty acid with a pleasant lemony odour and a number of its fractions gave a silver equivalent varying between 39-40 per cent. The properties of the acid agreed with those of geranic acid or one of its isomers. The non-volatile acid gave a purple coloured ammonium salt. The acid in fractions 2-4 is probably acrylic acid.

The ketone had a high lævo rotation and gave a liquid oxime and semicarbazone from which the ketone could not be regenerated. As the quantity present was small, it was not further examined.

Experimental.

The leaves collected in November were distilled in steam yielding a yellow oil (0·69 per cent. on the dry leaves). Another lot of leaves collected a fortnight later gave the same yield of oil. The authors desire to express their thanks to the forest department, Mysore, for the supply of leaves. The oils were thoroughly dried over anhydrous magnesium sulphate and had the constants given in table I. They showed no appreciable absorption with 4 per cent. sodium hydroxide.

TABLE I.

Sample No.	I	II
d_{30}^{30}	0·9317	0·9341
n_D^{30}	1·5114	1·5112
$(\alpha)_D^{30}$	−1·1°	−0·2°
Acid value	0·4	1·2
Ester value	9·2	13·4
Acetyl value	13·2	24·4

Distillation of the oil.—The oil (sample I, 358 g.) was fractionated five times with a Widmer column under diminished pressure, 50 mm. for the

lower boiling and 9 mm. for the higher boiling constituents, the final fractions obtained being as follows :—

TABLE II.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$(\alpha)_D$	Weight in grams	Yield per cent. on original oil
1	103°/50 mm.	0·8758	1·4710	+ 0·7	7·5	2·1
2	103	0·9046	1·4732	+ 0·2	7·5	2·1
3	103	0·9002	1·4726	+ 0·8	7·0	2·0
4	103	0·9028	1·4732	+ 0·4	17·0	4·7
5	103—103·5	0·9076	1·4742	± 0	16·0	4·5
6	103·5—104	0·9099	1·4754	± 0	16·0	4·5
7	104	0·9118	1·4771	± 0	17·0	4·7
8	104	0·9118	1·4762	± 0	17·0	4·7
9	104	0·9122	1·4784	± 0	17·0	4·7
10	104	0·9124	1·4766	± 0	16·0	4·5
11	104—104·5	0·9133	1·4802	— 0·1	17·0	4·7
12	104·5—105	0·9130	1·4786	— 0·1	20·0	5·6
13	105	0·9131	1·4792	— 0·1	16·0	4·5
14	105	0·9131	1·4805	— 0·1	16·0	4·5
15	105—106	0·9130	1·4864	— 0·1	16·0	4·5
16	106—110	0·9226	1·4952	— 0·1	10·0	2·8
17	78/9 mm.	0·9226	1·5032	— 0·4	2·0	0·5
18	78— 80	0·9226	1·5060	— 0·6	6·0	1·6
19	80— 90	0·9279	1·5292	— 2·3	6·0	1·6
20	90— 95	0·9328	1·5233	— 0·3	5·0	1·4
21	95— 98	0·9443	1·5335	— 3·8	4·0	1·2
22	120—122	0·9353	1·5120	—23·4	4·0	1·2
23	122—125	0·9247	1·5070	—42·3	2·0	0·5
24	180—187	1·015	1·5402	— 7·7	6·5	1·7
25	187—188	1·055	1·5457	+ 2·7	39·0	10·8
26	188—191	1·054	1·5466	+ 2·3	7·0	2·0
27	191	1·048	1·5470	+ 0·4	30·0	8·3

In the accompanying graph in Fig. 1 curves are drawn by plotting the physical constants, *viz.*, boiling points, specific gravities, refractive indices, and rotations against the percentage yield of the oil. The proportion of the main constituents α- and di-α-clausenan is shown by the boiling point curve. The curves show the number of minor constituents to be about three. Distillation divides the oil into three main groups 103-105/50, 80-125/9, 187-191/9, the first and the third consisting of the oxides and the intermediate one of ketones and esters.

Fraction 1 (*β-clausenan*).—This was mixed with corresponding fraction from sample II and re-fractionated at 53 mm., the following fractions (*a* and *b*) were obtained.

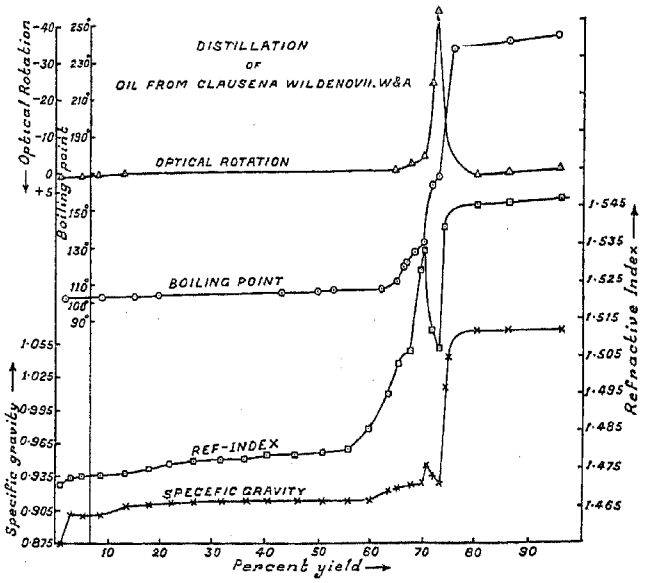


FIG. 1.

TABLE III.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$(\alpha)_D^{30}$
a	101°/53	0·8732	1·4706	+ 3·5
b	101–102/53	0·8902	1·4726	+ 1·0
x	99–100/50	0·8736	1·4710	+ 3·6
y	77–80/10	0·9137	1·4662	Acetyl value 199·2

The fraction *a* has the formula $C_{10}H_{14}O$ (C, 80·4; H, 9·3; $C_{10}H_{14}O$ requires C, 80·0; H, 9·3 per cent.). Treatment with magnesium methyl iodide gave no methane showing the absence of any alcohol. When fraction *a* (7·6 g.) was shaken with ferrocyanic acid, prepared by adding hydrochloric acid (10 c.c.) to an aqueous solution of potassium ferrocyanide (10 g.), a white solid was obtained which was washed with ether to remove adhering oil and decomposed by 10 per cent. sodium carbonate. The product (5·4 g.) was distilled over sodium and had the constants given in column *x* (C, 80·1; H, 9·6). It gave an acetyl value of 199·2 showing that it was a mixture of oxides, only one of which is acetylated. The acetyl derivative had the constants given in *y*. The pure acetyl derivative obtained in small quantity gives the transient purple coloration which becomes green,

purple and again green on further addition of bromine, as with the original oxide.

On addition of alcoholic potash to the acetyl derivative, a solid was formed which was not further examined, the quantity being small. This new optically active oxide which can also be acetylated, has been called *β*-clausenan. On account of the absence of hydroxylic compounds in the oil, it may be possible to quantitatively estimate *β*-clausenan by means of the acetyl value.

Fractions 2–4.—It was found that carbon in these fractions was lower by 0·5–1·0 per cent. than in the preceding or succeeding fractions. An ester was found to be present, fraction 2nd and 3rd having 35 and 30 as ester values. The liberated acid was unsaturated and the silver salt prepared from the ester contained silver 61·0 per cent.; silver acrylate requires Ag, 60·3.

Fractions 5–10.—Analysis of fraction 7 gave C, 80·6; H, 8·2; $C_{10}H_{12}O$ requires C, 81·0; H, 8·1. These fractions (97 g.) were mixed and fractionated over sodium at 49 mm. giving the following fractions (94 g.) which were all optically inactive.

TABLE IV.

	B.P.	d_{30}^{30}	n_D^{30}	$(R_L)_D$	Weight in grams
A	101·5°	0·9038	1·4733	45·99	26
B	101·5°	0·9050	1·4737	45·97	19
C	101·5°	0·9050	1·4737	45·97	32
D	101·5°	0·9062	1·4740	45·92	17

Analytical values for carbon and hydrogen were identical for A, B and D.

Purification of α-clausenan by liberation from ferrocyanic acid addition compound.—It was found that the fractions obtained above form addition compounds with ferrocyanic and ferricyanic acids. Pure ferrocyanic acid was prepared by adding concentrated hydrochloric acid to a saturated solution of potassium ferrocyanide. The precipitate was purified by twice dissolving in alcohol and re-precipitating with ether. The dry ferrocyanic acid (4 g.) was dissolved in water (20 c.c.) and shaken with fraction B (5 g.). The precipitate formed, was washed with ether to remove adhering oil. 0·8212 g. addition compound gave 0·130 g. Fe_2O_3 or Fe, 11·1 per cent. $H_4Fe(CN)_6 \cdot 2C_{10}H_{12}O$ requires Fe, 10·9 per cent.

The addition compound (4·0 g.) on decomposition with 10 per cent. sodium carbonate (20 c.c.) yielded α-clausenan (2·2 g.); $H_4Fe(CN)_6 \cdot 2C_{10}H_{12}O$ (4 g.) should give oxide (2·3 g.).

A pure sample of α-clausenan was re-treated with ferrocyanic acid and liberated; the properties remained the same showing that these acids have no action on the oxide:—

	B.P. 50 mm.	d_{30}^{30}	$d_{15\cdot5}^{15\cdot5}$	Change per degree C.	d_4^{30}
I Treatment with $H_4Fe(CN)_6$ ..	102°	0·9065	0·9155	0·00062	0·9010
II Do. ..	102°	0·9066	..	..	..

	$d_4^{15\cdot5}$	Change per degree C.	n_D^{30}	$(R_L)_D$	η_{30}	γ_{30}
I Treatment with $H_4Fe(CN)_6$ ..	0·9146	0·00094	1·4722	45·74	0·0085	29·1
II Do. ..	..	..	1·4722	45·74	..	..

Analysis gave C, 81·2; H, 8·2. The coefficient of cubical expansion has been found to be 0·00106 between 15° and 30°.

Addition compound with ferricyanic acid, $H_3Fe(CN)_6 \cdot 2C_{10}H_{12}O$.—Fraction 12 (29 g.) was shaken with ferricyanic acid, liberated from potassium ferricyanide (32 g.) and dilute sulphuric acid (2N, 120 c.c.) a white solid, which rapidly became dark green, was formed. The solid (47·00 g.) decomposed with 10 per cent. sodium carbonate gave the oxide (27·0 g.); $H_3Fe(CN)_6 \cdot 2C_{10}H_{12}O$ (47·0 g.) should give (27·1 g.). The pure oxide on distillation over sodium had the following properties, identical with those for the oxide liberated from $H_4Fe(CN)_6$; d_{30}^{30}, 0·9065; d_{50}^{50}, 0·8956; d_4^{50}, 0·8850; n_D^{30}, 1·4724.

Molecular weight determination.—0·3464 g. in 22·9806 g. of pure benzene gave a depression of 0·44°C. and 0·6600 in the same weight of solvent gave a depression of 0·81 (Found: M, 153, 157; Calculated for $C_{10}H_{12}O$, 148). The values obtained have been corrected for association by application of Fawsitt's formula (*J.C.S.*, 1919, **114**, 795). The uncorrected values are 171·4 and 177·4.

Colour reactions of α-clausenan.—A drop of a solution of bromine in acetic acid gave a transient purple coloration leaving the solution pale blue which on further addition becomes purple, then blue and finally deep green. The transition from purple to green seems to be very characteristic. Bromine in chloroform solution gives a transient purple coloration leaving the solution green, becoming dark green, blue, a beautiful purple and then green with more bromine solution. Strong mineral acids give a deep red coloration. Hydrogen chloride passed into an ethereal solution of the substance gives colour changes similar to those with bromine. The whole oil also gives these colour changes.

Action of bromine on α-clausenan.—When a solution of bromine in chloroform (2, 4 and 6 atoms) was added to an ice-cold solution of the substance, hydrogen bromide was evolved. No crystalline derivative could be isolated. The products were all dark, lustrous, amorphous bodies which did not melt even at 300°. The bromine content was very low in all the three specimens and varied between 19-20 per cent., $C_{10}H_{12}OBr_2$ requires 51·9 per cent. bromine. This behaviour is probably due to the resinifying action of bromine on the substance.

Properties of α-clausenan.—When α-clausenan (4·5 g.) was distilled at atmospheric pressure, it boiled at 177-178°/684 mm., the distillate (4 g.) had the properties given in column (*p*). It boiled without decomposition but showed effects of oxidation. Distillation in a current of nitrogen does not cause any change in properties. (*q*) gives the properties of a sample boiled with water for two hours and then distilled over sodium, (*r*) of a sample heated with water in a sealed tube for 6 hours at 170° and then distilled, (*s*) of a sample kept mixed with strong arsenic acid for 24 hours. In all these cases the original product was recovered practically unchanged showing that the oxide ring was quite stable.

	p	*q*	*r*	*s*
d_{30}^{30}	0·9120	0·9072	0·9065	0·9065
n_D^{30}	1·4752	1·4725	1·4722	1·4722

It was quite uneffected by boiling with acetic anhydride and unlike β-clausenan gave no acetyl derivative. In spite of the probable presence of four double bonds in the molecule, it was recovered unchanged by treatment with sodium and alcohol. On exposing α-clausenan (20 g.) in an atmosphere of oxygen for two days and then distilling, only (5 g.) came over at 8 mm., the remainder being an undistillable residue. The portion boiling at

130-140°/10 mm. had a formula $C_{10}H_{12}O_2$ (C, 73·2; H, 7·1; $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·3).

Fractions 11-15.—They were mixed (82 g.) and fractionated when α-clausenan (73 g.) was obtained.

Viscosity and surface tension of α-clausenan.—Viscosity was measured by means of an Ostwald viscometer calibrated with benzene at 30°. The time of flow for α-clausenan was 106·0 sec. and for water at the same temperature, 90·0 sec., both being averages of three readings which did not differ by more than 0·2 sec. The viscosity was found to be 0·0085 C.G.S., the relative viscosity being 1·068.

The surface tension was determined by the formula $\frac{\gamma_s}{\gamma_w} = \frac{h_s(d_s - \lambda)}{h_w(d_w - \lambda)}$ where γ_s and γ_w are surface tensions of the substance and water respectively, h_s and h_w, the difference in equilibrium levels in the capillary limb and the lower viscometer bulb, d_s and d_w being densities of the substance and water, and λ the density of air at 30° and 685 mm.; γ_w being known to be 71·4 from *Int. Crit. Tables*, h_s and h_w 28·85 and 64·15 mm. respectively, γ_s or the surface tension of α-clausenan was found to be 29·1 at 30° and 28·2 at 50°.

The parachor, $P = \frac{M\gamma^{\frac{1}{4}}}{d}$ was found to be 381·1 at 30° and 386·8 at 50° in agreement with the value (386·8) calculated from Sugden's data, revised by Mumford and Philips and Vogel (*J.C.S.*, 1929, **130**, 2112; 1934, **135**, 334).

Estimation of α- and β-clausenan in the whole oil by means of ferricyanic acid.—The oil (sample II, 5·1 g.) was shaken for 6 hours with $H_3Fe(CN)_6$ liberated from potassium ferricyanide (25 g.) and dilute sulphuric acid (2N, 55 c.c.). The precipitate obtained was decomposed by means of sodium carbonate when an oil (3·4 g. or 66·7 per cent.) was liberated, representing the mixture of α- and β-clausenan occurring in the oil.

Fractions 16-23.—Analysis of fraction 16 (C, 79·0; H, 9·2) showed that substances other than α-clausenan were present. No occurrence of alcohol could be detected. These fractions were found to contain varying proportions of ketones and esters along with oxides.

Fraction	Ester value	Ketones as $C_{10}H_{16}O$
18	9·1	0·1
19	10·4	0·3
21	18·0	0·5
22	—	25·0
23	5·8	

The optical activity appears to be due to the ketone and the rise in refractive index and specific gravity to an ester. Fraction 21 on saponification and removal of the acid had a pleasant odour. The ketones present did not yield any solid derivatives.

Acids from fractions 18-23.—The acids obtained by saponification were separated into volatile and non-volatile acids. The volatile acids had no fatty smell, but an agreeable odour like that of geranic acid. They decolourised bromine showing that they were unsaturated and a crystalline lead salt was obtained insoluble in ether. The volatile acids separated by steam distillation into three fractions contained nearly the same percentage silver, 39·0, 39·7, 40·0, giving 169, 164 and 162 respectively as equivalents for the acids. Analysis of the silver salt from first fraction of steam distillate gave C, 43·1; H, 5·4; $C_{10}H_{15}O_2Ag$ requires C, 43·6; H, 5·5. The acid is probably mainly geranic acid (equivalent 168) or one of its isomers.

Fractions 24-27 (*Di-α-clausenan*, $C_{20}H_{24}O_2$).—These fractions (62 g.) when distilled over sodium gave low boiling oxide (2 g.) and a large fraction (56 g.) boiling at a constant temperature of 188°/7 mm. The product after twice distillation over sodium had the following constants :—

$$d_{30}^{30}\ 1{\cdot}048;\ d_{50}^{50}\ 1{\cdot}025;\ d_{4}^{50}\ 1{\cdot}013;\ n_{D}^{30}\ 1{\cdot}5468;\ (\alpha)_{D}^{30} \pm 0;$$

$$\gamma_{30}\ 34{\cdot}5;\ \gamma_{50}\ 36{\cdot}1;\ \eta_{22}\ 1{\cdot}62.$$

It formed no addition compound with ferro- or ferri-cyanic acids unlike the other two oxides accompanying it. Analysis: C, 81·5; H, 7·9; $C_{20}H_{24}O_2$ requires C, 81·08; H, 8·16. By Rast's camphor method the substance (0·0655 g.) in camphor (0·4870 g.) gave a depression of 18·0°C. giving a molecular weight of 298·8, $C_{20}H_{24}O_2$ requires 296. The molecular refraction was found to be 89·58 while the calculated value for $C_{20}H_{24}O_2$ with seven double bonds and two furan oxygen atoms is 89·30. The parachor was found to be 704·2 at 30° and 716·7 at 50° not in agreement with the calculated value of 755·6 from Mumford and Philips' and Vogel's data. The formula appears to be in agreement for a dipolymer of α-clausenan and the substance has therefore been called di-α-clausenan. No similar polymer of β-clausenan has been detected. The optical activity of these fractions is due to contamination with traces of the optically active ketone.

With an acetic acid solution of bromine, a transient red colour is produced leaving the solution greenish yellow which with more bromine becomes brown, red and finally brown. In chloroform solution bromine gives a yellowish green coloration, changing to purple and finally deep red. Hydrogen chloride in ether gives similar colour changes as the chloroform solution of bromine. It also gives the Liebermann's colour reaction.

Di-α-clausenan is soluble in chloroform, ethylacetate, acetone, acetic acid, ether and benzene but sparingly in alcohol. It is uneffected by boiling with acetic anhydride and can be distilled without decomposition in nitrogen at atmospheric pressure. It is more rapidly oxidised by air or oxygen than α- or β-clausenan.

Summary.

The oil from the leaves of *Clausena willdenovii*, W. and A., has been found to consist almost entirely of three new bodies belonging to the furan group, α-clausenan $C_{10}H_{12}O$, di-α-clausenan $C_{20}H_{24}O_2$ and β-clausenan $C_{10}H_{14}O$. The former two have been obtained pure and their physical properties recorded. The addition compounds of α-clausenan with ferro- and ferricyanic acids $H_4Fe(CN)_6 \cdot 2C_{10}H_{12}O$, $H_3Fe(CN)_6 \cdot 2C_{10}H_{12}O$ which can be employed both for its purification and estimation, have been described. It is suggested that the acetyl derivative of β-clausenan can be employed for its estimation.