THE OCCURRENCE OF FURAN DERIVATIVES IN VOLATILE OILS—III.

β-Clausenan and γ-Clausenan.

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The volatile oil from the leaves of *Clausena Willdenovii*, W. and A. collected in winter has been shown to consist of three new compounds, α-, β- and di-α-clausenans belonging to the furan group.[1] The leaves of the same plant grown in a different locality and collected at the same time of the year, however, yielded a similar product but without any appreciable quantities of α-clausenan. The analytical constants of the three new oils (III, IV and V) and of the two previous samples (I and II) have been given in Table I and indicate apparent identity between them. The constants for the product obtained by extraction of the distillation water which dissolves out mainly the pleasant smelling esters have also been given. The new samples on fractionation behave like the previous specimens, as shown in Table II, three groups of products being obtained 104°/50 mm., 80–125°/10 mm., 190°/10 mm. The first fraction was found to be a mixture of β-clausenan and a new body hereafter called γ-clausenan which is the main constituent and is a clear colourless liquid having an odour of unripe mangoes. The next fraction consisted mainly of esters and ketones and the last of di-α-clausenan.

According to Wienhaus[2] the atomic refraction constant for furan oxygen is 1·2, being lower than for ethereal oxygen (1·642) in most other compounds. The molecular refractions of the clausenans taking the usual value and Wienhaus's constant are as follows :

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[1] *Proc. Ind. Acad. Sci.*, 1934, 1, 186.

[2] *Ber.*, 1920, **53**, 1660.

	d_4^{30}	n_D^{30}	$(R_L)_D$ Found	$(R_L)_D$ Calculated	
				0=1·643	0=1·2
α-Clausenan	0·9026	1·4722	45·96	45·96	45·51
γ-Clausenan	0·9050	1·4739	45·98	45·96	45·51
Di-α-Clausenan	1·0196	1·5468	89·95	90·18	89·29

It is found that the values are in good agreement with the usual value for ethereal oxygen. It has also been observed by Eisenlohr that the depression of molecular refraction observed in furan and pyrone decreases in their dimethyl derivatives and it is possible that in the higher homologues, this depression vanishes and the usual value for ethereal oxygen becomes valid.

The parachor was found to be 382·8 at 30° and 387·8 at 50° the calculated value being 386·8, the higher value at 50° indicating that γ-clausenan is an associated liquid. It has nearly the same viscosity as α-clausenan. The vapour pressures between 80–180°, Ramsay and Shield's constant and other properties have been determined and will be found in the experimental part. Dioxan was found to be unsuitable as a solvent for molecular weight determination of these compounds.

Pure γ-clausenan keeps well in the absence of oxygen and is miscible with most organic solvents. It has somewhat higher physical properties and differs from α- and β-clausenans in not forming an addition compound with either ferrocyanic or ferricyanic acids. It could be easily separated and purified by this process from β-clausenan with which it is mixed up. While α-clausenan was uneffected by sodium and alcohol, the γ-isomer was reduced to a tetrahydro-derivative. The reduction product gave the Liebermann colouration and with bromine in chloroform solution, the same colour changes as those observed with α-clausenan, showing the presence of the furan nucleus. No ketone was obtained by oxidation with potassium permanganate, as in the case of α-clausenan. Like most furan compounds γ-clausenan is also gradually resinified in the presence of acids and is uneffected by boiling acetic anhydride, alkalis and water. As γ-clausenan does not react with ferrocyanic acid, it was possible to obtain β-clausenan pure. Its properties along with those of its acetyl derivative have been described.

Experimental.

The analysis of oils obtained from three lots of leaves collected in winter from a different locality and immediately distilled have been given in Table I (III, IV and V), along with constants, for the samples previously examined, which show that they are similar.

TABLE I.

Sample No.	III	IV	V	I	II
d_{30}^{30}	0·9349	0·9333	0·9340	0·9317	0·9341
n_D^{30}	1·5129	1·5114	1·5112	1·5114	1·5112
$[\alpha]_D^{30}$	−1·6°	−2·1	−1·9	−1·1	−0·2
Acid value	0·3	0·2	0·4	0·4	1·2
Ester value	9·5	9·1	9·1	9·2	13·4
Acetyl value	22·2	23·7	20·1	13·2	24·4

Appreciable quantities of the oil were dissolved in the distillation water. The oil (10 g.) extracted from 8 litres of distillation water had the following properties : d_{30}^{30}, 1·086 ; n_D^{30}, 1·5182 ; acid value, 7·9 ; ester value, 220·1. The esters appear to be particularly soluble in water.

Distillation of the oil.—The oil (sample III ; 490 g.) was fractionated three times with an eight pear Young's column at 50 mm. in the first stage, and at 10 mm. later from a Claisen flask, the following fractions being obtained :

TABLE II.

Fraction	B.P.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in grams	Yield per cent. on original oil
1	101—103°/50 mm.	0·8984	1·4832	+ 0·9°	50	10·2
2	103—104	0·9107	1·4840	+ 0·4	100	20·4
3	104—105	0·9152	1·4882	+ 0·4	170	34·7
4	84—87/10 mm.	0·9226	1·4914	± 0	20	4·1
5	87—105	0·9304	1·5106	− 8·6	10	2·0
6	105—185	0·9350	1·5140	−18·2	5	1·0
7	188—193	1·060	1·5466	—	130	26·5

TABLE III.

γ-Clausenan		β-Clausenan	
Temperature °C.	Vapour pressure mm.	Temperature °C.	Vapour pressure mm.
82·0	27·0	70·0	19·5
95·0	44·0	85·0	38·0
102·0	52·5	97·0	65·5
112·0	74·0	99·0	72·0
119·5	106·5	104·0	82·0
125·5	127·0	125·0	172·0
129·0	145·0	131·0	207·5
135·0	180·0	138·0	258·0
139·0	210·0	148·0	348·0
143·0	235·0	154·0	412·5
144·5	265·0	158·0	458·0
151·0	314·0	161·0	496·0
156·0	360·0	168·0	597·0
159·0	394·0	171·0	644·0
163·5	449·0	174·0	696·0
165·5	474·5	176·0	734·5
171·0	548·0		
173·0	585·0		
175·0	607·5		
177·5	647·0		
180·0	684·0		

β-Clausenan.—Since the new samples were free from α-clausenan, it seemed possible that β-clausenan will be more easily obtained pure as the other compounds accompanying it do not react with ferrocyanic acid. Fraction I was treated with pure ferrocyanic acid and the addition compound decomposed with sodium carbonate and the liberated product was fractionated over sodium when β-clausenan having the following properties was obtained : b.p. 96–97/50 mm. ; d_{30}^{30}, 0·8805 ; d_4^{30}, 0·8768 ; d_{50}^{50}, 0·8701 ; d_4^{50}, 0·8589 ; $[\alpha]_D^{30}$, + 3·0 ; n_D^{30}, 1·4681 ; γ_{30}, 27·4 ; γ_{50}, 27·2 ; η_{30}, 0·090. Analysis : C, 79·46 ; H, 9·9 ; $C_{10}H_{14}O$ requires C, 80·0 ; H, 9·33. The vapour pressures have been given in Table III.

The parachor was 396·8 at 30° and 403·9 at 50° in fair agreement with the calculated value 397·4 according to Mumford and Philips and 406·4 according to Vogel.

Acetylation of β-clausenan.—β-Clausenan (5 g.) was boiled for an hour with acetic anhydride (10 c.c.) and sodium acetate (1·0 g.). The acetylated product distilled at 105°/32 mm. ; d_{30}^{30}, 0·9481 ; n_D^{30}, 1·4672 ; acetyl value 265, showing that the sample is quantitatively acetylated. Though β-clausenan is not as unsaturated as α-clausenan, it is more amenable to resinification and oxidation.

γ-Clausenan.—The major portion of the fractions failed to react with freshly prepared ferrocyanic acid. The unreacted portion (270 g.) on fractionation over sodium was found to be homogeneous and had the following properties given in (*a*), and (*b*) gives the properties of α-clausenan for comparison :

	B.P. at 50 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	$(R_L)_D$
(*a*)	103–104°	0·9089	1·4739	nil	45·98
(*b*)	102	0·9065	1·4722	,,	45·96

Analysis of (*a*) : C, 81·70 ; H, 8·40 ; $C_{10}H_{12}O$ requires C, 81·81 ; H, 8·18. It is not identical with α-clausenan having somewhat higher physical properties and is hereafter called γ-clausenan. It is uneffected by boiling with acetic anhydride, alkalis or water in a sealed tube. It gives the Liebermann test and with an acetic acid or chloroform solution of bromine, gives a purple colouration changing to blue and finally green, being similar in these respects to α-clausenan. Unlike the latter, however, γ-clausenan does not combine with ferrocyanic or ferricyanic acids.

Viscosity and surface tension of γ-clausenan.—They were measured by means of an Ostwald viscometer calibrated with benzene at 30° as in the case of α-clausenan. The time of flow for γ-clausenan was 105 seconds, being an average of four readings. The viscosity was found to be 0·0085 c.g.s.

The difference in the equilibrium levels in the capillary limb and the lower viscometer bulb was 29·6, 28·8 and 64·2 and 61 mm. for γ-clausenan and water respectively giving a surface tension of 29·92 at 30° and 29·10 at 50°.

The parachor was found to be 382·8 at 30° and 388·0 at 50°, the calculated values being 386·8 from Mumford and Philips and Vogel's data.[3]

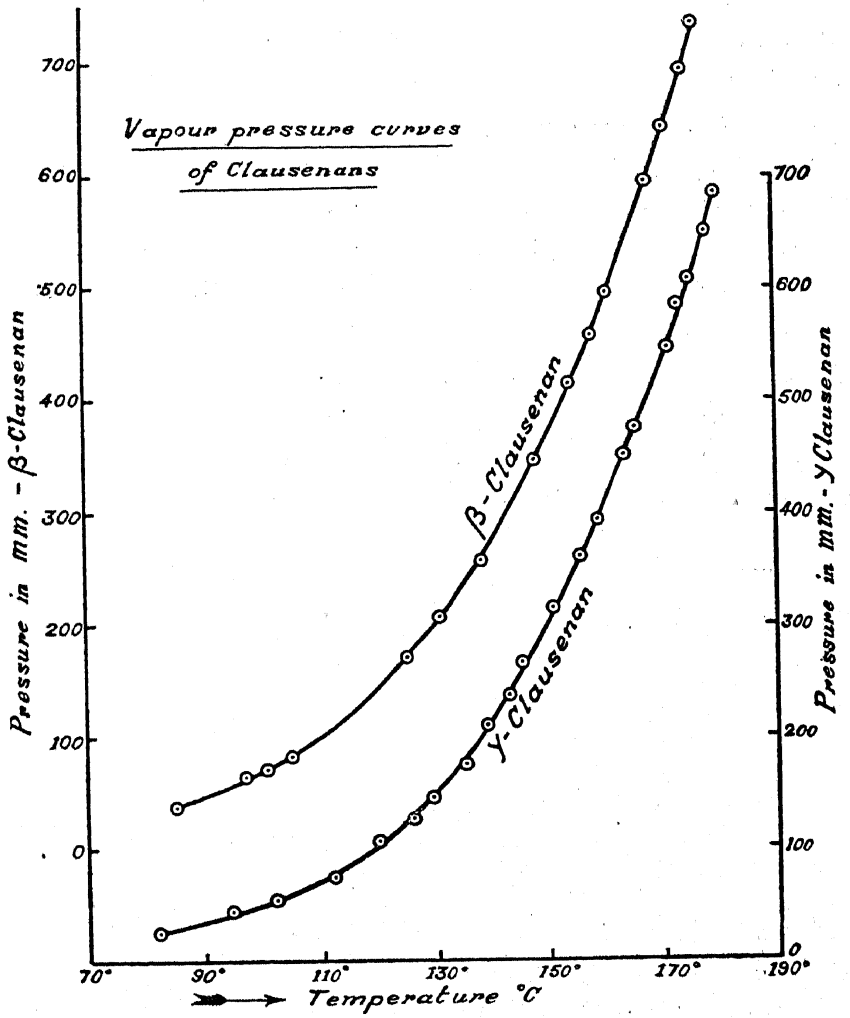

FIG. 1.

The molecular refraction was found to be 45·98, identical with the calculated value 45·96, taking for the furan oxygen Eisenlohr's value 1·643

[3] *J. C. S.*, 1929, **130**, 2112; 1934, **135**, 334.

for ethereal oxygen. If Wienhaus's value 1·2 is taken for the furan oxygen, the value for molecular refraction is depressed by 0·44.

The Ramsay and Shield's constant was found to be somewhat high being (*a*) 2·43 by application of Ramsay and Shield's equation, (*b*) 2·46 by Walden and Swinne's method.[4] The critical temperature by Guldberg rule is 412°. The molecular latent heat of vapourisation from Trouton's rule modified by Wartenburg[5] ($L = 7 \cdot 4T \times \log T$) was found to be 10,650 calories at 30°. The value from the formula

$$L = \frac{1 \cdot 985 T_1 T_2}{T_2 - T_1} l_n \frac{p_2}{p_1}$$

based on Clausius-Clapeyron equation was 10,730 calories at 98°C. The molecular volume, using Kopp's constants was 183·8, the experimental value being 148/0·7884 or 186·3.

The vapour pressures of γ-clausenan between 80-180° have been measured by the submerged bulb method of Smith and Menzies[6] and the values recorded in Table III. Fig. 1 shows the vapour pressure curves of the clausenans.

Reduction of γ-Clausenan.—On reduction with sodium and alcohol tetrahydro-γ-clausenan having the following properties was obtained: b.p. 105/100 mm.; d_{30}^{30}, 0·8957; n_D^{30}, 1·4698; C, 78·72; H, 10·22; $C_{10}H_{16}O$ requires C, 78·95; H, 10·52. α-Clausenan was not reduced by this process.

Oxidation with potassium permanganate.—No trace of the ketone $C_9H_{10}O$ obtained from α-clausenan was formed. The products were exclusively acidic and resinous and were not further examined.

Summary.

The analyses of three samples of the volatile oil from *Clausena Willdenovii*, W. & A. have been given. A component $C_{10}H_{12}O$, called γ-clausenan, isomeric with α-clausenan and belonging to the furan group has been isolated from the oil. Its physical properties as well as methods for separating it from α- and β-clausenans have been described. β-clausenan has been obtained pure and its properties determined.

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[4] *Z. Physik. Chem.*, 1913, **82**, 290.

[5] *Z. Electrochem.*, 1914, **20**, 444.

[6] *J. Am. Chem. Soc.*, 1910, **32**, 1448.