

# THE OCCURRENCE OF FURAN DERIVATIVES IN VOLATILE OILS—II.

$\alpha$ -Clausenan and Di- $\alpha$ -Clausenan.

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THE volatile oil from the leaves of *Clausena Willdenovii*, W. and A. has been shown to mainly consist of  $\alpha$ -,  $\beta$ - and di- $\alpha$ -clausenan belonging to the furan group.<sup>1</sup> The major constituent was  $\alpha$ -clausenan. The oil from the leaves grown in another locality was found not to contain any  $\alpha$ -clausenan but an isomeric substance,  $\gamma$ -clausenan. As a further supply of  $\alpha$ -clausenan in the near future seemed doubtful, it seemed desirable to put on record an account of the experiments that have been done with the limited quantity available.

$\alpha$ -Clausenan like some other furan derivatives gave an addition product with maleic anhydride, having the composition  $C_{14}H_{14}O_4$ , white crystalline needles melting at 85°. The corresponding acid  $C_{14}H_{16}O_5 \cdot 9H_2O$  (m.p. 98°) was obtained as white flakes from water. It lost  $7H_2O$  at 110° and the remaining two molecules at 140°. The anhydrous acid melted at 248° and could be directly obtained by recrystallising the hydrated acid from absolute alcohol or ether.

$\alpha$ -Clausenan with aqueous mercuric chloride at room temperature gave a white crystalline solid which did not melt but merely turned yellow at 180°. Its composition was  $C_{10}H_{10}O(HgCl)_2$  showing that two molecules of mercuric chloride had reacted.

During oxidation of  $\alpha$ -clausenan with an aqueous solution of ferrous sulphate, the furan nucleus was not effected. The reaction product consisted exclusively of a mixture of a primary and a tertiary alcohol of the same formula  $C_{10}H_{14}O_2$ . On acetylation the mixture of alcohols yielded the original hydrocarbon  $\alpha$ -clausenan and an acetate, the former being formed by dehydration of the tertiary alcohol. Both the alcohols and the acetate gave

<sup>1</sup> *Proc. Ind. Acad. Sci.*, 1934, 1, 184.

the Liebermann and the bromine colouration tests<sup>2</sup> showing the presence of the furan nucleus in them. The presence of a grouping  $R_1R_2C = CH_2$  is indicated in the side chain giving  $R_1R_2C(OH)CH_3$  (tertiary alcohol) and  $R_1R_2CHCH_2OH$  (primary alcohol). This was supported by the formation of a ketone  $C_9H_{10}O_2$  by oxidation with potassium permanganate. The ketone gave no solid derivatives but gave the colour reactions. Besides the ketone a small quantity of acid was obtained giving an anilide, m.p.  $154^\circ$  too small to be identified.

Dilute nitric acid (d., 1.12) had little action on  $\alpha$ -clausenan below  $30^\circ$ . With fuming nitric acid in acetic acid solution, a flocculent pale yellow precipitate was obtained in quantitative yield. It was found to be a nitro-ketone  $C_9H_9NO_4$  charring at  $130^\circ$ . With formic acid at  $0^\circ C$ . a resinous product boiling at  $240^\circ/2$  mm. was formed, no trace of di- $\alpha$ -clausenan being detected. Di- $\alpha$ -clausenan does not combine with maleic anhydride and gives not a tetra- but only a di-mercurial. It is reduced by sodium and alcohol unlike  $\alpha$ -clausenan. The significance of these results will be discussed in a subsequent communication.

#### Experimental.

$\alpha$ -Clausenan used in the following experiments was liberated from ferrocyanic acid addition compound and had the following properties:  $d_{30}^{30}$ , 0.9065;  $n_D^{30}$ , 1.4722;  $(R_L)_D$ , 46.02.

*Condensation of  $\alpha$ -clausenan with maleic anhydride.*—Maleic anhydride (7.0 g.) dissolved in dry benzene (50 c.c.) was gradually added to a benzene solution of  $\alpha$ -clausenan (9 g.). The solution gradually warmed up and turned yellow. After an hour at laboratory temperature, it was boiled on water-bath for two hours, the solution again becoming colourless. The solvent was distilled off and the oily residue slowly solidified. It was recrystallized from petrol-ether separating as stout needles melting sharply at  $85^\circ$ . It is sparingly soluble in cold water but readily dissolved in boiling water and alkalis. 0.1495 g. required 13.7 c.c. of 0.0885 N alkali giving an equivalent of 123.2 (calc. 123.0). The condensation anhydride rapidly decolorises a solution of bromine in chloroform. But no crystalline addition products of bromine could be isolated due to resinification. It is very soluble in most organic solvents except petrol-ether in which it is sparingly soluble.

*Hydrolysis of the anhydride.*—The anhydride (2 g.) was dissolved in just the theoretical quantity of 5 per cent. ice-cold aqueous potassium hydroxide and then acidified with ice-cold dilute acetic acid, when an acid (3 g.) separated as white flakes which washed with water and dried *in vacuo* melted at  $98^\circ$ .

<sup>2</sup> *Loc. cit.*

The use of mineral acids and higher temperature gave a resinous product which on recrystallisation gave a diminished yield of the pure acid. The acid (m.p.  $98^{\circ}$ ; 0.2868 g.) lost water (0.0868 g.) at  $110^{\circ}$  and further lost (0.0238 g.) at  $140^{\circ}$  giving an anhydrous acid melting at  $248^{\circ}$ . The hydrated acid (0.1370 g.) required for neutralisation alkali (7.2 c.c.; 0.0885 N) giving an equivalent of 214;  $C_{14}H_{16}O_5 \cdot 9H_2O$  gives an equivalent of 213. It loses 7 molecules of water at  $110^{\circ}$ , the remaining two molecules at  $140^{\circ}$ . Analysis of the anhydrous acid: C, 67.8; H, 5.5;  $C_{14}H_{16}O_5$  requires C, 68.3; H, 5.7 per cent. The acid (0.1297 g.) required alkali (9.7 c.c.; 0.0885 N) for neutralisation an equivalent of 132.4 (calc. 132). The anhydrous acid was also obtained by recrystallising the hydrated acid from absolute alcohol or ether when it was obtained in soft glistening needles, m.p.  $248^{\circ}$ .

*Oxidation of  $\alpha$ -clausenan with ferrous sulphate;  $\alpha$ -clausenyl alcohol.*— $\alpha$ -Clausenan (23 c.c.) was shaken for 8 hours with a saturated solution of ferrous sulphate (70 c.c.). The oily layer was removed, dried over magnesium sulphate and distilled when it had the following properties: b.p.  $88-89^{\circ}/28$  mm.;  $d_{30}^{30}$ , 0.9432;  $n_D^{30}$ , 1.4777; C, 73.0; H, 8.5;  $C_{10}H_{14}O_2$  requires C, 72.3; H, 8.5. This did not form any addition compound with ferro- or ferri-cyanic acids but gave the Liebermann's test and bromine colouration showing the presence of the furan ring. The acetyl value was 212 indicating only partial acetylation. By Sudborough-Zerewitinoff method<sup>3</sup> 0.1376 g. gave 22.4 c.c. at  $24^{\circ}C$ . and 683 mm. showing hydroxyl, 10.6 per cent.  $C_{10}H_{14}O_2$  requires 10.2 per cent. This indicated that the oxidation product was a mono-hydroxylic compound and that the furan ring was intact. On fractionation of the product at 28 mm. it was found to be a mixture, the following results being obtained:

TABLE I.

No.	B. P.	$d_{30}^{30}$	$n_D^{30}$
1	$-88.5^{\circ}$	0.9430	1.4775
2	$88.5-89$	0.9436	1.4778
3	$89-89.5$	0.9443	1.4778

By acetylation of the mixture of alcohols and distillation at 30 mm., the following fractions were obtained:—

<sup>3</sup> J. C. S., 1904, 85, 933; Ber., 1907, 40, 2023.

<i>a</i>	−90°	0.9046	1.4730
<i>b</i>	90–93	0.9050	1.4732
<i>c</i>	93–98	0.9319	1.4682
<i>d</i>	98–100	0.9524	1.4684

Fractions *a* and *b* on distillation over sodium had the following properties: b.p. 104°/53 mm.;  $d_{30}^{30}$ , 0.9067;  $n_D^{30}$ , 1.4722. It combined with ferro-cyanic acid and was identical in every respect with  $\alpha$ -clausenan.

*Fraction d*: Analysis: C, 69.8; H, 7.8;  $C_{12}H_{16}O_3$  requires C, 69.2; H, 7.7. On saponification with alcoholic potash it gave an alcohol having the following properties: b.p. 89–90°/30 mm.;  $n_D^{30}$ , 1.4779;  $d_{30}^{30}$ , 0.9441 in good agreement with fraction 3, Table I. This primary alcohol has been called  $\alpha$ -clausenyl alcohol. This could be quantitatively acetylated and gave a liquid phthalic ester when treated with phthalic anhydride in benzene solution. The re-acetylated product had the following properties: b.p. 98–102°/30 mm.;  $n_D^{30}$ , 1.4683;  $d_{30}^{30}$ , 0.9522. The proportion of the two alcohols formed during oxidation with ferrous sulphate varied in different experiments. The  $\alpha$ -clausenyl alcohol as well as the acetate resinified far more rapidly than  $\alpha$ -clausenan itself.

*Oxidation of  $\alpha$ -clausenan with potassium permanganate.*—To  $\alpha$ -clausenan (10 c.c.) in acetone (100 c.c.) potassium permanganate (20 g.) was gradually added in small quantities, the temperature being maintained between 0–5° C. The mixture was poured into water and manganese dioxide filtered off. The neutral product had the following properties: b.p. 95–96°/55 mm.;  $d_{30}^{30}$ , 0.9285;  $n_D^{30}$ , 1.4531; C, 71.2; H, 7.0;  $C_9H_{10}O_2$  requires C, 72.0; H, 6.7. It reacted quantitatively with hydroxylamine, giving a liquid oxime, no solid ketonic derivatives being obtained. The filtrate was concentrated and acidified when a small quantity of resinous product was obtained. It yielded an anilide, m.p. 154° but the quantity available being small it was not further investigated.

*Action of nitric acid on  $\alpha$ -clausenan.*—Dilute nitric acid (d., 1.12) has little action at laboratory temperature, tarry products being formed, when the temperature was raised. With fuming nitric acid, better results were obtained. To  $\alpha$ -clausenan (6.4 g.) dissolved in glacial acetic acid (32 c.c.) and cooled in a freezing mixture fuming nitric acid (d., 1.52; 4 c.c.) dissolved in glacial acetic acid (20 c.c.) was gradually added under vigorous stirring

according to Marquis.<sup>4</sup> On pouring into water a micro-crystalline yellow solid separated (9.0 g.). It is soluble in chloroform, ethyl acetate, acetone, ether, benzene and insoluble in petrol-ether and water. It dissolves in alkalis and is purified by solution in chloroform and reprecipitation with petrol and then chars at 130° C. Analysis: C, 54.9; H, 4.9; N, 7.4;  $C_9H_9NO_4$  requires C, 55.1; H, 4.6; N, 7.2. It formed a semicarbazone which did not melt below 350°; N, 21.0;  $C_{10}H_{12}O_4N_4$  requires N, 22.22.

*Mercuration of  $\alpha$ -clausenan.*—To a solution of mercuric chloride (2 g.) and sodium acetate (4 g.) in water (50 c.c.) cooled by ice was added  $\alpha$ -clausenan (1.5 g.) in alcohol (8 c.c.).<sup>5</sup> A solid began separating after a few minutes, the solution turning slightly red. The oil gradually disappeared after 48 hours. The pale-buff coloured precipitate was filtered off and dried and was purified by extracting with large quantities of hot acetone. The colourless crystalline solid (0.6 g.) thus obtained did not melt but became yellow at 180°. It turned black with mineral acids, alkalis and sodium carbonate. Mercury was estimated after solution in strong nitric acid and titration against standard thiocyanate solution; Hg, 65.4;  $C_{10}H_{11}O.HgCl$  requires Hg, 52.3,  $C_{10}H_{10}O(HgCl)_2$  requires Hg, 64.9 thus showing that it was a di-chloro-mercury derivative.

#### *Di- $\alpha$ -Clausenan.*

The product used in the experiments below had the following properties: b.p. 188°/7 mm.;  $d_{30}^{30}$ , 1.048;  $n_D^{30}$ , 1.5468.

*Action of fuming nitric acid.*—To di- $\alpha$ -clausenan (5 g.) dissolved in glacial acetic acid (30 c.c.) cooled in a freezing mixture, a glacial acetic acid (20 c.c.) solution of fuming nitric acid (4 c.c.) was gradually added under stirring during an hour and then poured over ice. A yellow solid similar to the one from  $\alpha$ -clausenan separated. It charred at 140° and dissolved in most organic solvents except petrol-ether. It was purified by reprecipitating it from a chloroform solution; C, 55.1; H, 5.0; N, 7.4;  $C_{18}H_{18}N_2O_8$  requires C, 55.1; H, 4.6; N, 7.2.

*Mercuration of di- $\alpha$ -clausenan.*—To mercuric chloride (4 g.) and sodium acetate (8 g.) dissolved in water (100 c.c.) was added di- $\alpha$ -clausenan (3 g.) in alcoholic solution. A solid separated in comparatively poor yield and after purification with acetone weighed 0.4 g. A resin was formed as a subsidiary product, which could be removed by washing the mercurial with chloroform in which the resin was found to be very soluble. The mercurial turned yellow at 150°. Analysis: Hg, 53.7;  $C_{20}H_{22}O_2(HgCl)_2$  requires Hg, 52.4.

<sup>4</sup> *Ann. Chem. Phys.*, 1905, 4(viii), 196.

<sup>5</sup> *J. Amer. Chem. Soc.*, 1933, 55, 3303.

Di- $\alpha$ -clausenan showed no tendency to combine with maleic anhydride. Unlike  $\alpha$ -clausenan it could be reduced by sodium and ethyl alcohol, a product having the following properties being obtained: b.p. 100–101°/4 mm.;  $d_{30}^{30}$ , 0.9354;  $n_D^{30}$ , 1.4906.

*Summary.*

The condensation product of  $\alpha$ -clausenan and maleic anhydride and the corresponding acid have been described. Di-chloromercury derivatives have been prepared both from  $\alpha$ -clausenan and di- $\alpha$ -clausenan. By oxidation with ferrous sulphate, a primary alcohol ( $\alpha$ -clausenyl alcohol,  $C_{10}H_{14}O_2$ ) is formed along with an isomeric tertiary alcohol which is easily dehydrated to  $\alpha$ -clausenan. Two positions, one of which is  $\alpha$ , appear to be free in the furan nucleus of  $\alpha$ -clausenan. The formation of a ketone  $C_9H_{10}O_2$  and a nitroketone  $C_9H_9NO_4$  from it indicates the presence of a terminal methylene group.