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PAPERS

DEPARTMENT OF CHEMISTRY

Volume 1 1939 Numbers 11, 12, 13, and 14

11. The Reduction of Tagetone to Tagetol

BY

T. G. H. JONES, D.Sc., A.A.C.I.

12. The Constitution and Synthesis of Conglomerone

BY

F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

13. Essential Oils from the Queensland Flora

Part XVII.—The Essential Oil of *Evodia littoralis* and the Occurrence of a New Phenolic Ketone

BY

F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

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PART XVII.—THE ESSENTIAL OIL OF EVODIA LITTORALIS AND THE OCCURENCE OF A NEW PHENOLIC KETONE.

By

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ESSENTIAL OILS FROM THE QUEENSLAND FLORA, PART XVII.

THE ESSENTIAL OIL OF EVODIA LITTORALIS AND THE OCCURRENCE OF A NEW PHENOLIC KETONE.

By F. N. LAHEY, M.Sc., and T. G. H. JONES, D.Sc., A.A.C.I.

Evodia littoralis grows in quantity on the ranges in the Springbrook district near the New South Wales border. The young trees springing up on the areas cleared for farming are covered with dense foliage and thus lend themselves to the collection of leaves for steam distillation.

The essential oil from the leaves has the characteristic odour of the olefinic terpene, ocimene, which is the principal constituent, other constituents being d-α-pinene, sesquiterpenes, a sesquiterpene alcohol and a phenol.

The occurrence of this phenol in relatively large amounts is of particular interest as the work so far carried out seems to indicate that it has not been previously isolated. It is obtained in the form of a bright yellow solid m.p. 84°C. Its alcoholic solution gives with ferric chloric a green colouration turning red on the addition of sodium bicarbonate solution. It readily forms a mono-methyl and a mono-acetyl derivative both of which are white. The phenol and the methyl-phenol yield derivatives with 2:4 dinitro-phenyl-hydrazine indicating the presence of a carbonyl radical.

The phenol for which we propose the name evodionol, appears to have the formula $C_{15}H_{18}O_4$. It contains a methoxyl as well as a carbonyl and phenolic group while the nature of the fourth oxygen atom has not yet been determined.

EXPERIMENTAL.

Leaves weighing 180 lb. yielded 182 cc. of oil on steam distillation.

This oil possessed the following constants:—

$d_{15\cdot5}$ .. .. = ·8487
$[\alpha]_D$ .. .. = + 16·5
n_D^{20} .. .. = 1·4860
Ester Value .. .. .. = 0
Acetyl Value .. .. .. = 36

The oil was then washed with sodium carbonate and sodium hydroxide solutions in turn. Nothing was extracted with the sodium carbonate but the sodium hydroxide wash on acidification yielded a yellow phenol (9 grams) which was purified by recrystallisation from petroleum ether (charcoal).

The residual oil was dried and then fractionally distilled at 2 mm. pressure. After several refractionations the following head fractions were obtained:—

(1.) .. .. 32–33° C.
$d_{15\cdot5}$ ·8555
$[\alpha]_D + 41\cdot7$
n_D^{20} 1·4662

(2.) .. .. $36\frac{1}{2}$–37° C.
$d_{15\cdot5}$ ·8039
$[\alpha]_D + 3\cdot$
n_D^{20} 1·4822

(3.) .. .. 60–70° C.
$d_{15\cdot5}$ ·9232
$[\alpha]_D + 7.$

(4.) .. .. 82–85° C. (over sodium).
$d_{15\cdot5}$ ·9100
$[\alpha]_D - 2$
n_D^{20} 1·4950

(5.) .. .. 92–95° C. (over sodium).
$[\alpha]_D + 17\cdot$
$d_{15\cdot5}$ ·9286
n_D^{20} 1·4982

(6.) .. .. 108–112° C.
$d_{15\cdot5}$ ·9765
$[\alpha]_D - 5$
n_D^{20} 1·4970

Fraction (1) was treated with maleic anhydride for the removal of ocimene by the method of Birch.[1] The fraction was treated with excess of maleic anhydride in acetone and allowed to stand twenty-four hours. The acetone was then removed and dilute caustic soda added to decompose any excess maleic anhydride. The residual oil was steam distilled. The procedure had to be repeated to remove the last trace of ocimene. The remaining oil then had

$d_{15\cdot 5}$ .. .. ·8621
$[\alpha]_D$ .. .. + 48·6

This was identified as d-α-pinene by oxidation with neutral permanganate to pinonic acid, the semicarbazone of which melted at 204°C. The high optical rotation of this fraction indicated a second constituent in this fraction, probably d-limonene, but this could not be identified.

Only two cubic centimetres of fraction (3) were available. This contained a sesquiterpene and a sweet-smelling alcohol resembling linalol.

Fractions (4) and (5) consisted of sesquiterpenes and fraction (6) a sesquiterpene alcohol. The first two were treated with selenium at 280°C. Each yielded a small quantity of an azulene the picrate of which melted at 121°C. Neither cadalene nor eudalene could be found in the recovered oils.

Fraction (6) was refluxed with formic acid for one hour. The sesquiterpene recovered had

$d_{15\cdot 5}$ ·9297
n_D^{20} 1·4988

This is probably the same sesquiterpene as occurs in fraction (5).

The Phenol, Evodionol.—After recrystallisation from petroleum ether, evodional melted sharply at 84°C. With ferric chloride a dark green colouration is produced which turns red on the addition of bicarbonate solution suggestive of the catechol nucleus. It readily forms a methyl and an acetyl derivative which are white and melt at 78°C. and 66°C. respectively.

Evodionol forms an amorphous 2 : 4 dinitro-phenyl-hydrazone m.p. 217°C. while the methyl evodionol derivative is in the form of red needles m.p. 157°C.

Analyses of these various derivatives have been carried out and are recorded below.

Evodionol—

Found	C. 68·1	H. 6.7	N. (2 : 4 dinitro-phenyl-hydrazone).
	68·1	6·4	..
	68·	6·8	12·8
$C_{15}H_{18}O_4$ requires	C. 68·7	H. 6·9	N. 12·7

Methyl-evodionol—

Found	C. 69·6	H. 7·4	N. 12·7
$C_{16}H_{20}O_4$ requires	C. 69·6	H. 7·2	N. 12·3

Acetyl-evodionol—

Found	C.	66·9	H.	6·6
$C_{17}H_{20}O_5$ requires	C.	67·1	H.	6·6

Molecular Weight (Rast) 314 $C_{17}H_{20}O_5$ requires 304.

The elimination of methyl iodide in methoxyl determinations was very sluggish, the first sign of reaction being after one and a-half hours' heating. After seven hours' treatment a value of 10·1 per cent. methoxyl was obtained. One methoxyl group in $C_{15}H_{18}O_4$ requires 11·9. It is thought that longer treatment will raise the figure obtained. It is thus seen that the analytical results are in fair agreement with the formula $C_{15}H_{18}O_4$.

Further work which, it is hoped, will throw light on the constitution of evodionol is at present in progress and will be published at a later date.

REFERENCE.

(1) A. J. Birch. J. and Proc. Roy. Soc. N.S.W. 1937, p. 54.