



University of Queensland

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.

14. Optically Pure 1- α -Phellandrene

BY

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

Price: Two Shillings

DEPARTMENT OF CHEMISTRY.

VOLUME 1.

1939.

NUMBER 12.

THE CONSTITUTION AND SYNTHESIS OF
CONGLOMERONE.

By

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

Department of Chemistry, University of Queensland.

DATE OF PUBLICATION:

25TH SEPTEMBER, 1939.

THE CONSTITUTION AND SYNTHESIS OF CONGLOMERONE.

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

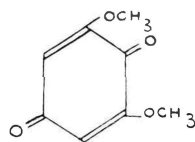
In a previous paper¹ the occurrence of a white crystalline solid in the essential oil from *Eucalyptus conglomerata* was recorded. The preliminary work on this solid then published indicated a possible formula to be $C_{13}H_{18}O_4$, while methoxyl determinations pointed to the presence of three methoxyl groups. These results have now been confirmed.

The substance, for which we propose the name conglomerone, has been shown to be a ketone. It forms a 2:4 dinitro-phenyl-hydrazone although not readily, precipitation of the hydrazone taking place only after twelve hours' standing. It does not yield a semicarbazone or an oxime.

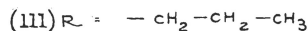
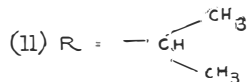
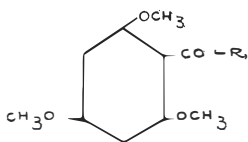
Oxidation experiments with permanganate were unsuccessful. In the cold no action took place but on heating, oxidation proceeded readily with the formation of oxalic acid. Oxidation with Beckmann's chromic acid mixture yielded a bright yellow crystalline substance m.p. 252°C. identified as dimethoxy-quinone (1) by comparison with a sample of dimethoxy-quinone prepared by the oxidation of phloroglucinol-trimethyl-ether with dichromate.

Treatment with alcoholic sodium hydroxide at 160°C. yielded a neutral, a phenolic and a volatile acidic product. The neutral product has not yet been identified. The phenol after methylation was found to be phloroglucinol-trimethyl-ether, the alcoholic sodium hydroxide having brought about partial demethylation as well as elimination of the side chain. Analysis of the silver salt of the volatile acid showed it to be a butyrate or isobutyrate.

On the basis of this evidence it appeared as though conglomerone would be represented by either formula (11) or (111). Of these, formula (11) appeared the more probable in view of the steric hindrance exhibited towards ketonic reagents.



(1)



The synthesis of (11) was carried out and the product was found to be identical with conglomerone. The 2:4 dinitro-phenyl-hydrazones gave no depression in a mixed melting point. The crystals of synthetic and natural conglomerone were examined and found identical by Dr. W. H. Bryan, of the Geology Department, University of Queensland, to whom we express our thanks.

EXPERIMENTAL.

Isolation of Conglomerone.—By the steam distillation of 760 lb. of leaves and terminal branchlets of *Eucalyptus conglomerata* 870 cc. of oil separated from which 98 grams of conglomerone crystallised after the more volatile constituents had been distilled off. A further 17 grams were obtained by salting out the aqueous distillate from steam distillation. The crude solid was purified by recrystallisation from light petroleum (charcoal) from which white needles separated m.p. 62–62.5°C.

Found C, 65.4 H, 7.8 methoxyl, 39 per cent.

$\text{C}_{13}\text{H}_{18}\text{O}_4$ requires C, 65.5 H, 7.6 methoxyl, 39.1 per cent.

for three methoxyl groups.

2:4 dinitro-phenyl-hydrazone.—Conglomerone dissolved in alcohol was treated with excess of a solution of 1 gram of 2:4 dinitro-phenyl-hydrazone and 2 cc. of concentrated sulphuric acid in 20 cc. of alcohol. After this solution had stood for twelve hours the precipitate was filtered off and recrystallised from alcohol. The hydrazone melted at 164°C.

Found: Nitrogen 13.4 per cent.

The 2:4 dinitro-phenyl-hydrazone of $\text{C}_{13}\text{H}_{18}\text{O}_4$ requires 13.4 per cent. N.

Oxidation with Dichromate.—One gram of conglomerone was heated under reflux with 50 ccs. of Beckmann's chromic acid mixture. A bright yellow crystalline solid separated on cooling. This was filtered off and recrystallised from water, m.p. 252°C.

Found: C, 57.1

H, 4.7

$C_8H_8O_4$ requires C, 57.2 and H, 4.6.

Dimethoxy-quinone was prepared by oxidising trimethyl-phloro-glucinol (trimethoxy-benzene) with Beckmann's chromic acid. This was isolated as yellow needles insoluble in cold water, m.p. $252^\circ C$. Mixed melting point with the above showed no depression.

Treatment with Alcoholic Sodium Hydroxide.—Conglomerone (15 grams) was added to a solution of 8 grams of sodium hydroxide in 90 per cent. alcohol. This was sealed in a stainless steel bomb and heated for four hours at $160^\circ C$. The product was poured into water and extracted with ether. The residue was treated with carbon dioxide to liberate the phenol which was extracted with ether. The residue was acidified with dilute sulphuric acid and steam distilled, yielding a volatile acid, the silver salt of which, on analysis, gave 54.9 per cent. of silver. Silver isobutyrate requires 55.4 per cent. silver.

The principal product here was the neutral product, a thick liquid boiling at $130^\circ C$. at 2 m.m. This has not yet been identified.

The phenol after the ether was removed, was obtained as a yellow liquid boiling at $90^\circ C$. at 2 m.m. It was methylated with dimethyl sulphate and caustic soda. The product readily crystallised, and after drying on a plate and recrystallising from petroleum-ether, it melted at $51^\circ C$. and showed no depression on admixture with a sample of phloroglucinol-trimethyl-ether.

Synthesis of Conglomerone.—Seventeen (17) grams of phloroglucinol were dissolved in 170 grams of methyl alcohol (dry) and saturated with hydrogen chloride. The mixture was then refluxed for one hour, again saturated with HCl, and allowed to stand overnight. The alcohol was then distilled off and the residue methylated with dimethyl sulphate and caustic soda. The trimethyl-phloroglucinol was isolated by steam distillation. To a mixture of 1 gram of trimethyl phloroglucinol and .8 gram of isobutyryl chloride in 5 cc. of dry carbon disulphide was added 1 gram of freshly sublimed ferric chloride. It was then refluxed for one hour, the carbon disulphide layer poured off and the residue decomposed with dilute hydrochloric acid. This was extracted with ether, dried, the ether distilled off and the residue steam distilled. The white crystalline solid obtained on recrystallisation from petroleum ether (charcoal) melted at $62-62.5^\circ C$. and showed no depression on admixture with natural conglomerone.

Found: C, 65.3 H, 7.4.

The 2:4 dinitro-phenyl-hydrazone of the synthetic material was formed as described for the natural body and the melting point and mixed melting point found identical with that of the natural conglomerone derivative. Conglomerone has thus been shown to be isobutyryl-phloroglucinol-trimethyl-ether, (phlorisobutyrophenone-trimethyl-ether).

REFERENCE.

- (1) Proc. Roy. Soc. Queensland, 1938, pp. 10-13.
-