Tetrahedron Letters No. 5, pp. 289-291, 1963. Pergamon Press Ltd.
Printed in Great Britain.

TETRAHYDROFRANKLINONE

P. Margaret Brown, J.S. Burton and R. Stevens.
Brewing Industry Research Foundation, Nutfield, England.

(Received 17 November 1962)

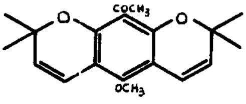
THE essential oil of Acradenia franklinii (Kippist) contains a mixture of ketones based on a phloroglucinol nucleus.[1] Our interest in one of these, franklinone, arose out of the close similarity of the proposed[1] structure (I) to a degradation product of the hop β-acid, colupulone (II; R = Pr^i) studied earlier in these laboratories.[2,3] Acid degradation of colupulone gave two pyrans (III; R = Pr^i) and (IV; R = Pr^i, R' = H); the former being converted into the latter by treatment with concentrated sulphuric acid. Methylation of the latter using diazomethane gave (IV; R = Pr^i, R' = Me) which had light absorption, λ_{max} 275 mμ (log ϵ 3.6), in agreement with that reported for tetrahydrofranklinone,[1] a lower homologue.

---

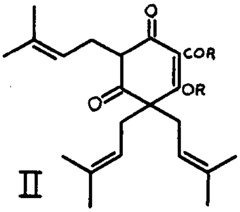
[1] M.E. Baldwin, I.R.C. Bick, A.A. Komzak and J.R. Price, Tetrahedron **16**, 206 (1961).

[2] G.A. Howard, J.R.A. Pollock and A.R. Tatchell, J. Chem. Soc. 174 (1955).

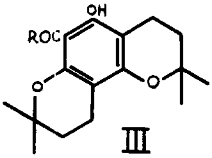
[3] B.H. Arnold, J.J.H. Hastings and T.K. Walker, Chem. & Ind. 323 (1955).



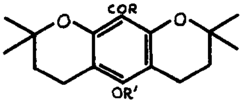
I



II



III



IV

We now report the synthesis of tetrahydrofranklinone by a route analogous to that used to prepare the lupulone degradation products. The reaction of phloroacetophenone with two moles of 1-bromo-3-methylbut-2-ene in dry chloroform afforded the pyran (III; R = Me), m.p. 117-8°, ν_{max} 1600 cm^{-1} (chelated C=0), which was rearranged by treatment with concentrated sulphuric acid into the pyran (IV; R = Me, R' = H), m.p. 159-159.5°, ν_{max} 3400 cm^{-1} (OH) 1650 cm^{-1} (aryl C=0). Methylation of the latter compound using diazomethane gave tetrahydrofranklinone (IV; R = R' = Me), m.p. 141.5-142°, undepressed on admixture with authentic tetrahydrofranklinone; λ_{max} 275 mμ (log ε 3.6). The infra-red spectra of the authentic and the synthetic tetrahydrofranklinone were identical.

Acid degradation of synthetic[4] acetolupuphenone

---

[4] W. Riedl, Ber. 85, 692 (1952).

(II; R = Me) afforded the same two pyrans, (III; R = Me) and (IV; R = Me, R' = H).

Attempts to prepare franklinone itself by bromination and subsequent dehydrobromination of tetrahydrofranklinone have so far been unsucessful. All the new compounds described analysed satisfactorily.

Acknowledgements - We thank Dr. I.R.C. Bick for the mixed m.p. determination and comparison of the infra-red spectra of the synthetic and authentic samples of tetrahydrofranklinone and Dr. A.H. Cook, F.R.S., for his encouragement.