

β -TRIKETONES

III. XANTHOSTEMONONE*

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Summary

Xanthostemone, $C_{12}H_{16}O_3$, by its properties and by oxidation reactions is shown to have formula I.

I. INTRODUCTION

Steam distillation of the air-dried leaves of *Xanthostemon oppositifolius* Bail., a member of the family Myrtaceae, gave in 0.22 per cent. yield an oil which was almost completely soluble in sodium carbonate solution. On distillation a new substance, xanthostemone, $C_{12}H_{16}O_3$, was obtained. This closely resembled in its general properties dehydroangustione (II) (Birch and Elliott 1956). It gave a red ferric test, the ultraviolet absorption had maxima at λ 231 m μ , $\log \epsilon$ 4.03; λ 280 m μ , $\log \epsilon$ 3.82 (cf. dehydroangustione λ 230 m μ , $\log \epsilon$ 4.05; λ 282 m μ , $\log \epsilon$ 3.76). It contained no OMe and the Kuhn-Roth estimation indicated less than 1 C-Me. However, other members of this series (Birch and Elliott 1956) gave similar low values and it seems probable that 2 C-Me are present. The infra-red absorption curve showed a series of strong bands in the region of 6-7.5 μ as with other β -triketones (Birch 1951). It gave a 2,4-dinitrophenylhydrazone, $C_{18}H_{20}O_6N_4$, m.p. 239 °C.

Oxidation of xanthostemone with alkaline hypobromite gave rise to a lower fatty acid and an acid $C_7H_{10}O_4$, m.p. 132 °C, which is probably identical with 2,2-dimethylglutaconic acid (III), m.p. 134 °C (Perkin and Smith 1903), of which none was available for comparison. Hydrolysis with 50 per cent. sulphuric acid gave what is almost certainly isobutyric acid, recognized by paper chromatography, together with a colourless substance $C_8H_{10}O_2$, m.p. 150.5 °C, with the properties of a β -diketone, and which is to be formulated as IV. Its ultraviolet absorption at λ_{\max} 233 m μ , $\log \epsilon$ 4.04; λ_{\max} 280 m μ , $\log \epsilon$ 3.79 is similar to that of the trimethylcyclohexendione similarly produced from dehydroangustione. Confirmation of the presence of *gem*-dimethyl groups in the ring was provided by oxidizing xanthostemone with permanganate to obtain dimethylmalonic acid. Hydrogenation of xanthostemone, followed by hydrolysis, gave a β -diketone, $C_8H_{12}O_2$, m.p. 104 °C, indicating further the presence of a double

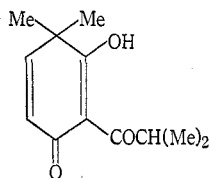
* Birch and Elliott (1955) may be regarded as Part II of this series.

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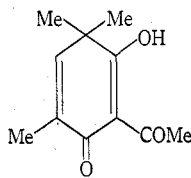
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bond in the ring. These data can be accommodated only on the basis of formula I for xanthostemone.

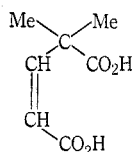
Xanthostemone is therefore a homologue of dehydroangustione (II), and its biosynthesis is presumably similar (cf. Birch and Elliott 1956). It is of interest that the initial acid is *isobutyric* rather than acetic acid, and that only two methyl groups are present in the ring. There can be no doubt in this case as to the position of the double bond, and its discovery adds further weight to the biosynthetic hypotheses already put forward (Birch, Elliott, and Penfold 1954; Birch and Elliott 1956).



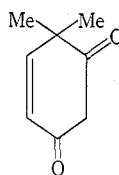
(I)



(II)



(III)



(IV)

II. EXPERIMENTAL

Air-dried leaves and terminal branchlets (20 lb) of *Xanthostemon oppositifolius*, "Southern Penda", obtained from Como, via Ku Ku, Queensland, were steam distilled for 9 hr. The distillate (40 gal) was extracted with ether to yield 20 c.c. of oil giving an intense red ferric test. The oil was extracted with aqueous sodium bicarbonate, carbonate, and hydroxide successively, the bulk being soluble in the carbonate solution. Acidification and distillation gave xanthostemone, b.p. 95–102 °C/0.8 mm (mainly at the higher temperature), $[\alpha]_D^{20}$ 0° (c, 2.37 in chloroform), n_D^{24} 1.5112 (Found: C, 70.1; H, 7.9; OMe, nil; C-Me, 5.6%. Calc. for $C_{12}H_{14}O_3(2C-Me)$: C, 69.2; H, 7.7; C-Me, 14.4%). It was recovered unchanged after refluxing for 2 hr with aqueous sodium hydroxide (10%). The 2,4-dinitrophenylhydrazone formed orange-red needles, m.p. 239 °C from a large volume of methanol (Found: C, 55.4; H, 5.4%. Calc. for $C_{18}H_{20}O_6N_4$: C, 55.7; H, 5.2%).

(a) *Oxidation of Xanthostemone*.—(i) *Hypobromite*. The substance (100 mg) in aqueous sodium hydroxide (4 c.c.; 10%) was reacted at room temperature for 1 hr with bromine (240 mg) in sodium hydroxide solution (10 c.c.; 10%). The bromoform was removed, excess hypobromite destroyed by the addition of sodium sulphite, and the solution acidified. Several extractions with ether, and extraction of the ether with sodium bicarbonate and acidification gave an acid, m.p. 132 °C from benzene-light petroleum (b.p. 60–90 °C) (Found: C, 53.0; H, 6.1%. Calc. for $C_7H_{10}O_4$: C, 53.2; H, 6.4%).

(ii) *Permanganate*. Xanthostemone (1 g) in acetone (40 c.c.) was treated with finely powdered potassium permanganate (1.2 g) in small portions with shaking. After 1 hr, water

(4 c.c.) was added and a further 2 g of potassium permanganate. After 3 hr, a further 1 g of permanganate was added and the mixture left overnight. The manganese dioxide was removed by filtration and washed with water (40 c.c.), the extract being added to the evaporated acetone solution. After filtration, the aqueous extract was evaporated under reduced pressure to 6 c.c. and acidified. Extraction with ether (10 × 10 c.c.) and evaporation gave dimethylmalonic acid recrystallized from benzene-light petroleum (b.p. 60–90 °C), m.p. 187 °C undepressed by an authentic specimen.

(b) *Hydrolysis of Xanthostemone*.—Xanthostemone (1 g) was heated on a steam-bath with aqueous sulphuric acid (4 c.c.; 50%). The mixture was diluted with water and extracted with ether, and the ether shaken with sodium bicarbonate solution to give (A) ether-soluble and (B) acidific fractions. Fraction A on evaporation of the ether gave a colourless solid, m.p. 105.5 °C, from benzene-light petroleum (b.p. 60–90 °C) which is apparently 4,4-dimethylcyclohexan-1,3-dione (Found: C, 69.1; H, 7.2%. Calc. for $C_8H_{10}O_2$: C, 69.5; H, 7.3%). Fraction B was acidified and steam distilled. The distillate, smelling strongly of lower fatty acid, was extracted with butanol and chromatographed on paper by the method of Lindqvist and Storgards (1953), the distances travelled being measured relative to acetic acid (R_A); possible acids were run for comparison. Several experiments gave consistent results; one is quoted: isobutyric acid, R_A 2.20; hydrolysis acid, R_A 2.20; isovaleric acid, R_A 3.00; n-butyric, R_A 2.30. The acid is therefore almost certainly isobutyric acid.

(c) *Hydrogenation of Xanthostemone*.—Xanthostemone (400 mg) in ethanol was hydrogenated with Adams's catalyst until hydrogen (44 c.c.; 1 mole) had been absorbed. After evaporation of the solvent the residual oil was hydrolysed as above with sulphuric acid (50%) to give colourless crystals, m.p. 104 °C, from benzene-light petroleum (b.p. 60–90 °C) presumably 4,4-dimethylcyclohexan-1,3-dione (Found: C, 68.2; H, 8.7%. Calc. for $C_8H_{10}O_2$: C, 68.5; H, 8.6%).

III. ACKNOWLEDGMENTS

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