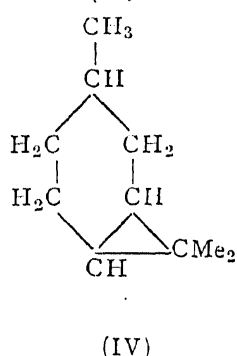
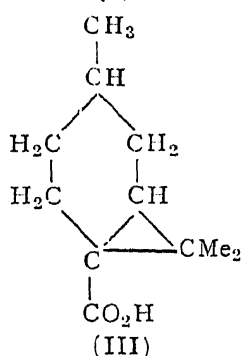
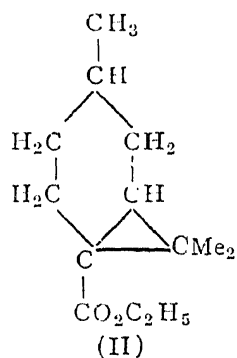
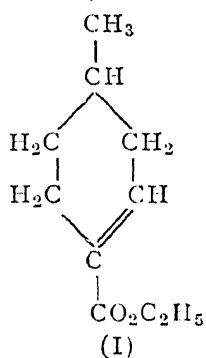


## Synthesis of Carane.

IN the present communication, the synthesis of carane starting from a *cyclohexene* derivative, possessing a methyl group in position 1, and a double bond between the carbon atoms in positions 3 and 4, is described. The starting substance was ethyl  $\Delta^1$ -tetrahydro-*p*-toluate, obtained in an improved yield according to the method of



Bardhan<sup>1</sup> starting from *p*-methyl *cyclohexanone*. The unsaturated compound (I) reacts with dimethyl-diazomethane on being allowed to stand at 0° during two weeks to yield the bicyclo (0 : 1 : 4)-heptane derivative (II) (b.p. 150 – 160°/6 mm.) giving on hydrolysis with 5 per cent. alcoholic potassium hydroxide the corresponding carboxylic acid (III), m.p. 104–105°; Eq. Wt. Found : 181.2; required, 182. The acid on being distilled with ZnO–BaO under reduced pressure gives a compound which from its boiling point (Found : 161°/684 mm.; known, 169°/750 mm.), refractive index (Found : 1.4553; known, 1.4567) and the characteristic smell appears to be carane (IV). It is to be mentioned that the present synthesis constitutes the first total synthesis of a bicyclic compound of the carane series.

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## Rottlerin—Part IV.

IN Part III, we have advocated the view that rottlerin is best represented by the formula  $C_{31}H_{30}O_8$  containing five hydroxyl groups which are methylated by dimethyl sulphate and potassium bicarbonate in acetone solution. Since then, McGookin, Percival and Robertson<sup>1</sup> have stated that all their previous published data are equally explainable on the basis of  $C_{30}H_{28}O_8$  (pentahydroxy) formula as against  $C_{33}H_{30}O_9$  (hexahydroxy) formula which they once considered to be possible.<sup>2</sup> Although it is difficult to pronounce a final opinion on this question, yet our results, notably the oxide and the nitrosite, are best explained on the basis of a  $C_{31}$  formula for rottlerin. Hoffmann and Fari<sup>3</sup> advocated a  $C_{31}$  formula mainly on the analysis of the sodium salt. Therefore, the present indications are that probably rottlerin is  $C_{31}$  but as we have already mentioned this question will not be solved finally before more data accumulates.

Robertson *et al*<sup>1</sup> described a substance  $C_{20}H_{18}O_4$  obtained by the alkaline hydrolysis (barium hydroxide) of rottlerin, which they called rottlerone. We found<sup>4</sup> that the hydrolysis of tetrahydrorottlerin with aqueous alcoholic hydrochloric acid gave a substance  $C_{20}H_{22}O_4$  ( $\pm 1 CH_2$ ) which we suggested might be identical with tetrahydrorottlerone described by Robertson *et al*. We have now methylated our product and find it to be so. In this connection we wish to state that this substance  $C_{20}H_{22}O_4$  is obtained in a much greater yield by the acid hydrolysis described by us (3.2 g. from 8.0 g. of tetrahydrorottlerin) whilst Robertson *et al* obtained 5 to 6 gr. from 20 g. of tetrahydrorottlerin by the sodium hydroxide hydrolysis. Under the following conditions, the yield stated above can be easily obtained.

Tetrahydrorottlerin (8 g.) in alcohol (400 c.c.), hydrochloric acid (d. 1.14, 80 c.c.) and water (40 c.c.) was heated for 26 hours. The substance was obtained by filtering the mixture hot as an insoluble powder which crystallised from ethyl acetate. If in the above experiment the reaction mixture is cooled and diluted after 8 hours heating, a light brown substance is precipitated which is soluble in sodium bicarbonate and behaves like an unstable acid. Owing to the ease of decomposition, it has not been possible to get it in a pure form but it is certain that it is an acid and also this very substance

<sup>1</sup> *J.C.S.*, 1935, 478.