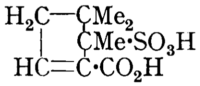
100. *The Constitution of Sulphocamphylic Acid.*

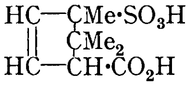
By J. R. Lewis and J. L. Simonsen.

Sulphocamphylic acid, first prepared by Walter (*Ann. Chim.*, 1843, **9**, 177) by the action of sulphuric acid on camphoric acid, was investigated subsequently by Kachler (*Annalen*, 1873, **169**, 179), Damsky (*Ber.*, 1887, **20**, 2959), Koenigs and Hoerlin (*ibid.*, 1893, **26**, 812, 2045), Koenigs and Meyer (*ibid.*, 1894, **27**, 3466), and Perkin, jun. (J., 1898, **73**, 799; 1903, **83**, 835).

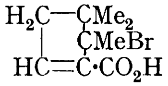
As the outcome of his detailed studies of the reactions of the sulphonic acid, which he prepared also by the action of sulphuric acid on *iso*lauronolic acid, Perkin suggested that it was most probably represented by (I): later, Aschan ("Chemie der Alicyklischer Verbindungen," p. 572), without adducing any fresh experimental evidence, advanced the alternative formula (II) as being more in accord with its formation from camphoric acid.



(I.)



(II.)



(III.)

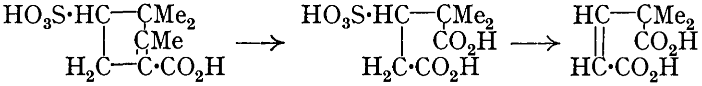
Although the formation of α-camphylic acid (dehydro-α-campholytic acid) on alkali fusion would be explained readily by (II), its conversion into β-camphylic acid (dehydro*iso*lauronolic acid) and into *iso*lauronolic acid are more in accord with (I). Neither formulation, however, accounts for the observation recorded by Koenigs and Hoerlin (*loc. cit.*, p. 2045) that the so-called sulphopimelic acid, $C_7H_{12}O_7S$, prepared by Kachler (*loc. cit.*, p. 181) by the oxidation of sulphocamphylic acid with nitric acid, decomposed on heating at 160—170° to give sulphur dioxide and terebic acid.

It was shown by Perkin (*loc. cit.*, p. 827) that when sulphocamphylic acid bromide was heated at 155° it gave an unsaturated bromo-acid, bromodihydro-β-camphylic acid, $C_9H_{13}O_2Br$, to which he assigned the structure (III). Oxidation of this acid with ozone has now been found to give a liquid bromoketo-acid (*semicarbazone*, m. p. 190°), which on further oxidation with sodium hypobromite yields bromoform and *trans*-αα-dimethylglutaconic acid, elimination of hydrogen bromide accompanying the oxidation of the acyl group. The degradation to αα-dimethylglutaconic acid can only be explained if the bromo-acid is represented by either (IV) or (V); the bromoketo-acid would then be either (VI) or (VII).


(IV.) (VI.) (V.) (VII.)

The structure (V), 5-bromo-2 : 3 : 3-trimethyl-Δ^1-*cyclo*pentene-1-carboxylic acid, has, however, been assigned already to *iso*bromodihydro-β-camphylic acid, which gives on ozonolysis, followed by oxidation with sodium hypobromite, *as*-dimethylsuccinic acid (Lewis and Simonsen, J., 1936, 735). It follows, therefore, that bromodihydro-β-camphylic acid must be 4-bromo-2 : 3 : 3-trimethyl-Δ^1-*cyclo*pentene-1-carboxylic acid (IV) and the bromoketo-acid must be (VI), the formulation of the latter as a β-bromo-acid accounting for the facile loss of hydrogen bromide in the presence of alkali.

These results suggested that sulphocamphylic acid must be 4-sulpho-2 : 3 : 3-trimethyl-Δ^1-*cyclo*pentene-1-carboxylic acid (VIII), a structure in accord with its conversion by alkali into α- and β-camphylic acids, but still irreconcilable with its degradation to terebic acid. We have therefore re-examined the oxidation of sulphocamphylic acid with nitric acid under the conditions used by Koenigs and his collaborators. We can confirm the formation of dimethylmalonic and oxalic acids, but we find that the so-called sulphopimelic acid (or sulpho*iso*propylsuccinic acid) gives on pyrolysis, not terebic acid, but a mixture of *cis*- and *trans*-αα-dimethylglutaconic acids (X). It follows, therefore, that sulphopimelic acid must be β-*sulpho-αα-dimethylglutaric acid* (IX), the reactions proceeding in accordance with the following scheme :


(VIII.) (IX.) (X.)

The recognition of sulphocamphylic acid as a sulpho*iso*lauronolic acid shows that the sulphonation of *iso*lauronolic acid proceeds without molecular rearrangement and it must be assumed that the primary action of sulphuric acid on camphoric acid is to give α-campholytic acid, which, as is well known, isomerises in the presence of mineral acids to *iso*lauronolic acid.

An attempt was made to confirm the structure assigned to sulphocamphylic acid by the ozonolysis of the acid itself and of its methyl ester. From the latter a stable *ozonide*, m. p. 83—85°, was obtained, but this ozonide and that obtained from the acid gave on decomposition viscid oils from which no crystalline derivatives could be prepared. The presence of an acyl group was, however, proved by the formation of bromoform on oxidation with sodium hypobromite. When the oil from the decomposition of the ozonide of sulphocamphylic acid was heated at 130—140°, it gave an unsaturated dibasic *acid*, $C_{16}H_{20}O_4$, m. p. 145—147°. This acid is possibly related to the diketo-acid, dicampherylic acid, $C_{18}H_{20}O_6$, obtained by Perkin by the oxidation of sulphocamphylic acid with potassium permanganate.

EXPERIMENTAL.

4-*Bromo*-2 : 3 : 3-*trimethyl*-Δ^1-cyclo*pentene*-1-*carboxylic Acid*.—The following modification of Perkin's method (*loc. cit.*, p. 827) was found convenient. Dry sulphocamphylic acid bromide (4 g.), heated in xylene (20 c.c.) at 125—135°, slowly dissolved, sulphur dioxide being evolved. If this temperature was exceeded, the yield was much diminished. After evolution of gas had ceased (2 hours), the solution was filtered from a little carbonaceous matter, and the xylene removed in steam, in which the bromo-acid was only slowly volatile. The bromo-acid (3 g.), which separated from the cooled aqueous solution, was recrystallised from dilute formic acid and then had m. p. 128—129°.

Oxidation of 4-*Bromo*-2 : 3 : 3-*trimethyl*-Δ^1-cyclo*pentene*-1-*carboxylic Acid.*—The acid (1 g.) in ethyl acetate (15 c.c.) was oxidised with ozone at 0°; formaldehyde was not detected in the issuing gases. After removal of the solvent under diminished pressure, the ozonide was decomposed by warming with water and the heavy oil which separated was extracted with ether. Removal of the solvent gave an oil, the *semicarbazone* of which separated from dilute acetic acid in plates, m. p. 190° (Found: C, 37·0; H, 5·6; N, 14·2; Br, 26·7. $C_9H_{16}O_3N_3Br$ requires C, 36·7; H, 5·4; N, 14·3; Br, 27·2%).

The bromoketo-acid (1·5g.) was dissolved in dilute sodium carbonate solution and treated with an excess of sodium hypobromite at 0°; bromoform separated immediately. After 1 hour the bromoform was removed, the excess of hypobromite destroyed by sulphur dioxide, and the solution acidified and repeatedly extracted with ether. Evaporation of the solvent gave an oil, which crystallised on trituration with hydrochloric acid. The solid, recrystallised from hot water, formed leaflets, m. p. 169—171° alone and in admixture with *trans*-αα-dimethylglutaconic acid (Found: C, 53·4; H, 6·6. Calc. for $C_7H_{10}O_4$: C, 53·2; H, 6·3%).

Oxidation of Sulphocamphylic Acid.—The acid (6 g.), suspended in ethyl acetate (50 c.c.) at 0°, dissolved when ozone was passed in. After removal of the solvent the ozonide was suspended in water (10 c.c.), a clear solution being obtained on gentle warming. This gave on evaporation a viscid oil, which contained free sulphuric acid and gave with sodium hypobromite a copious precipitate of bromoform; attempts to prepare crystalline derivatives were unsuccessful. When the oil (2 g.) was heated at 130—140° for 3·5 hours, a gum was obtained, which dissolved in hot water (5 c.c.); the filtered solution on cooling deposited a brown solid. The *acid* crystallised from water (charcoal) in needles, m. p. 145—147° [Found: C, 69·3; H, 7·7; *M*, 265 (Rast), 276 (titration). $C_{16}H_{20}O_4$ requires C, 69·6; H, 7·3%; *M*, 276]. The acid was unstable to potassium permanganate in alkaline solution, but it was not oxidised by percamphoric acid. Catalytic hydrogenation in alcoholic solution with a palladium catalyst was slow and indicated the presence of three ethylenic linkages.

Ozonolysis of methyl sulphocamphylate (1 g.) in carbon tetrachloride (15 c.c.) at 0° gave an oil, from which, after warming with water for 30 minutes, ether extracted an *ozonide* crystallising from methyl alcohol in cubes, m. p. 83—85° (Found: C, 42·4; H, 5·8; S, 10·3. $C_{11}H_{18}O_8S$ requires C, 42·6; H, 5·8; S, 10·4%). Prolonged digestion of the ozonide with water gave a homogeneous solution, from which no crystalline products could be separated.

Pyrolysis of β-*Sulpho*-αα-*dimethylglutaric Acid.*—The acid, prepared as described by Koenigs and Hoerlin (*loc. cit.*), was heated under diminished pressure at 160—170°; sulphur dioxide was evolved and a small quantity of a crystalline solid (*A*) distilled. The brown crystalline residue in the distilling flask was dissolved in sodium carbonate solution, filtered from carbonaceous matter, and acidified. The acid, which separated, crystallised from water in leaflets, m. p. 170—171° alone and in admixture with *trans*-αα-dimethylglutaconic acid (Found: C, 53·0; H, 6·6; *M*, 162. Calc.: C, 53·2; H, 6·3%; *M*, 158). The acid (*A*), crystallised from hydrochloric acid and then from benzene, had m. p. 131° and was probably *cis*-αα-dimethylglutaconic acid, for which Perkin and Smith (J., 1903, **83**, 16) record m. p. 135° (Found: C, 53·2; H, 6·3%; *M*, 161).

The authors are indebted to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries Ltd. for grants.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, February 2nd*, 1937.]