The Chemistry of Hop Constituents. Part VI.* The Structure of Cohumulone.

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Cohumulone, $C_{20}H_{28}O_5$, closely resembles humulone. Thus, hydrogenolysis of cohumulone leads to cohumuloquinol and, thence, oxidation *via* the quinone affords *iso*cohumulinic acid. Similarly alkaline hydrolysis of cohumulone gives cohumulinic acid, $C_{14}H_{20}O_4$, which contains an *iso*butyryl and a 3-methylbut-2-enyl side-chain and is thus a lower homologue of humulinic acid. Cohumulone and humulone therefore differ structurally only in that they include respectively an *iso*butyryl and an *iso*valeryl side-chain.

A PRELIMINARY account of the properties of cohumulone which occurs together with humulone in many varieties of hops (Howard and Tatchell, *J. Inst. Brew.*, 1953, 491) has already been given (Howard and Tatchell, *Chem. and Ind.*, 1953, 436) and the present paper amplifies these earlier reports. Cohumulone, which has been obtained only as an oil, behaves as a single component on counter-current distribution in *iso*octane–phosphate buffer at pH 8·0 or in *iso*octane–phosphate buffer at pH 7·2 containing 15% of methanol. Its lead salt has a composition consistent with the formulation $C_{20}H_{26}O_5Pb$ from which the formula $C_{20}H_{28}O_5$ may be inferred for cohumulone itself, as compared with $C_{21}H_{30}O_5$ for humulone. This result agrees both with the equivalent of 351 found experimentally and with the results of Rigby and Bethune (*J. Amer. Chem. Soc.*, 1952, **74**, 6118). Cohumulone thus appears formally to be a lower homologue of humulone. The infra-red absorption spectra of the two compounds are similar as are also their ultra-violet spectra (Harris, Howard, and Pollock, *J.*, 1952, 1906; Howard and Tatchell, *loc. cit.*) and this circumstance, together with the close chemical similarities between the two compounds, suggests that they contain similar functional groups similarly arranged.

Hydrolysis of cohumulone by boiling N-alkali gave results which present an interesting comparison with those obtained with humulone (cf. Harris, Howard, and Pollock, *loc. cit.*), in both cases *iso*butyraldehyde and 4-methylpent-3-enoic acid being obtained. The hydrolysate of cohumulone contained however a new compound, cohumulinic acid, m. p. 79—80°, corresponding to the humulinic acid, m. p. 92°, obtained from humulone. Cohumulinic acid, $C_{14}H_{20}O_4$, has one methylene group less than humulinic acid (Harris, Howard, and Pollock, *loc. cit.*). It was readily hydrogenated catalytically to dihydro-cohumulinic acid, $C_{14}H_{22}O_4$. Ozonolysis confirmed the presence of a double bond, acetone being obtained as the sole volatile carbonyl product.

The ultra-violet and infra-red spectra and the general reactions of cohumulinic acid are respectively so similar to those of humulinic acid as to indicate that they contain the same central nucleus and functional groups and differ only in their side-chains. When dihydro-cohumulinic acid was oxidised by alkaline hypobromite, *iso*butyric acid was obtained in good yield. Dihydrocohumulinic acid and thus presumably cohumulinic acid and cohumulone therefore contain an *iso*butyryl side-chain in place of the *iso*valeryl group in humulone and its derivatives.

The nature of the alkyl side-chain of cohumulinic acid remained to be determined. Oxidation of dihydrocohumulinic acid with periodate gave an oil which was hydrolysed by alkali to 3-methylbutan-2-one, 6-methylheptan-2-one, and *iso*butyric acid. This further indicates the close similarity of dihydrohumulinic and dihydrocohumulinic acids and confirms the presence in the latter of both an *iso*butyryl and a 3-methylbutyl group. This, together with the formation of acetone during the ozonolysis of cohumulinic acid, implies that the latter contains the same 3-methylbut-2-enyl side-chain as humulinic acid (cf. Harris, Howard, and Pollock, *loc. cit.*). Cohumulinic acid must consequently be (II), its dihydro-derivative (III), and cohumulone itself (I).

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* Part V, *J. Inst. Brewing*, 1953, 480.

On two occasions the attempted hydrogenation of cohumulinic acid gave, instead of the usual dihydrocohumulinic acid, a new acidic compound, $C_{14}H_{24}O_3$, m. p. 162—163° (cf. Howard and Tatchell, *loc. cit.*). This material has only one ultra-violet absorption band, whereas humulinic and cohumulinic acid and their dihydro-derivatives have the two bands usually exhibited by compounds containing the triketomethine grouping. The spectrum of the compound $C_{14}H_{24}O_3$ is, however, similar to that of 4-hydroxy-2-methyl-*cyclo*pentane-1 : 3-dione (Orchin and Butz, *J. Amer. Chem. Soc.*, 1943, **65**, 2296) and of 2-ethyl-4-*n*-propyl*cyclo*pentane-1 : 3-dione (Woodward and Blout, *ibid.*, p. 562). The available evidence is thus consistent with the formulation of this material as 4-hydroxy-5-3'-methylbutyl*cyclo*pentane-1 : 3-dione and this is supported by the fact that the compound rapidly reduces one molar equivalent of periodate. Investigations are in progress to elucidate the conditions under which this compound is produced and to establish its structure.

Cohumulone consumes three molar equivalents of hydrogen when hydrogenated in methanolic palladous chloride. The colourless solution so obtained absorbed one equivalent of oxygen to give a solution from which the purple crystalline cohumulo-quinone, $C_{15}H_{20}O_5$ (IV), was isolated and characterised as its azine with *o*-phenylene-diamine. Hypobromite oxidation of the quinone led to an *iso*cohumulinic acid, $C_{14}H_{20}O_4$ (V), which is hydrolysed by alkali to 3-3'-methylbutyl*cyclo*pentane-1 : 2 : 4-trione (VI) which is obtained by a similar degradation of humulone (Harris, Howard, and Pollock, *loc. cit.*).

The conclusion to be drawn from these investigations is that cohumulone differs from humulone only in containing an *iso*butyryl in place of the *iso*valeryl group.
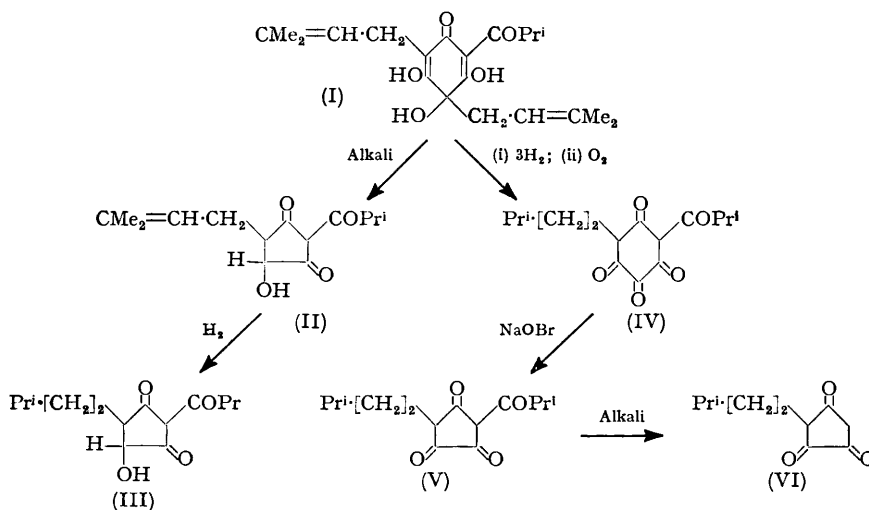
The results obtained by ozonolysis of cohumulone, however, appeared at one time to be inconsistent with the above conclusion. Oxidation of humulone by ozone has been reported (Carson, *J. Amer. Chem. Soc.*, 1951, **73**, 4652; Riedl, *Brauwiss.*, 1951, 51) to yield acetone as the sole volatile product in a yield indicating the presence of two *iso*propylidene groups in humulone. The volatile fission products resulting from the ozonolysis of cohumulone gave, however, a mixture of 2 : 4-dinitrophenylhydrazones. Various attempts to resolve the mixture having failed recourse was had to reverse-phase partition chromatography with benzene and formamide as the stationary and the mobile phase respectively (Howard and Tatchell, *Chem. and Ind.*, 1954, 219). Under these conditions the mixture was separated into the 2 : 4-dinitrophenylhydrazones of acetaldehyde and acetone, the yield of the latter, however, accounting only for that required by the presence of one *iso*propylidene group. On re-examination of the ozonolysis of humulone it was found that this reaction also gave acetaldehyde and acetone. Detailed study finally revealed that

ozonolysis at —58° in chloroform with the avoidance of prolonged reaction converts both humulone and cohumulone into acetaldehyde and acetone, although under these conditions the yield of the latter in each case was sufficient to indicate the presence of two *iso*-propylidene groups. The formation of acetaldehyde remains without explanation.

The similarity between cohumulone and humulone being established as stated above, the main reactions of cohumulone (I) may be summarised as in the formulæ. The easy hydrogenolysis of carbon–carbon bonds observed in the sennoside series (Stoll, Becker, and Helfenstein, *Helv. Chim. Acta*, 1950, **33**, 313) suggests by analogy that the hydrogenolysis of structures such as (I) is not unreasonable. Such formulations are therefore considered less open to the criticisms made earler (Harris, Howard, and Pollock, *loc. cit.*).

EXPERIMENTAL

Cohumulone was prepared by the counter-current method (Howard and Tatchell, *loc. cit.*). The solvent system *iso*octane–0·5M-phosphate buffer of pH 8·0 which was used earlier and resulted in the separation of cohumulone and humulone after about 200 transfers was incapable of handling large quantities of material as formation of emulsions led to loss of cohumulone by aerial oxidation. However, the system *iso*octane–0·5M-potassium phosphate buffer of pH 7·2 containing 15% of methanol proved more satisfactory in handling up to 30 g. of humulone–cohumulone mixtures.

Cohumulone had $[\alpha]_D$ —195° in MeOH and an equiv. wt. of 351 (Calc. for $C_{20}H_{28}O_5$, 348). The *lead* salt was prepared in the usual way (Found : C, 43·2; H, 4·9; Pb, 36·7. $C_{20}H_{26}O_5Pb$ requires C, 43·4; H, 4·7; Pb, 37·4%).

Alkaline Hydrolysis of Cohumulone.—(*a*) Cohumulone (720 mg.) in ethanol (10 c.c.) and N-sodium hydroxide (13 c.c.) was boiled under reflux in a stream of nitrogen for 1·5 hr., the effluent gases being passed into aqueous 2 : 4-dinitrophenylhydrazine hydrochloride. The hydrolysate was concentrated to 10 c.c. by distillation, the distillate being collected in 2 : 4-dinitrophenylhydrazine hydrochloride solution. The combined 2 : 4-dinitrophenylhydrazones were extracted with benzene and chromatographed on alumina in benzene. One main band only was observed which was eluted and the material obtained by concentration was recrystallised from methyl*cyclo*hexane, to give *iso*butaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 177—179°. The residual solution from the alkaline hydrolysis was acidified with dilute sulphuric acid and distilled. The acid was extracted from the distillate with ether and converted in the usual way into *p*-bromophenacyl 4-methylpent-3-enoate, m. p. and mixed m. p. 91—92°.

(*b*) Cohumulone (4·6 g.) in ethanol (9 c.c.) and N-sodium hydroxide (63 c.c.) was heated under reflux in a stream of nitrogen for 1·5 hr. and the solution concentrated to 50 c.c. Carbonyl compounds in the distillate and the effluent gases were converted into their 2 : 4-dinitrophenyl-hydrazones as before. The latter were extracted with benzene, and the solution chromatographed on silica gel (Merck). The main band gave material which, after recrystallisation from methanol, had m. p. 182—183° undepressed on admixture with *iso*butaldehyde 2 : 4-dinitrophenylhydrazone; no other hydrazone was isolated. The alkaline hydrolysate was acidified at 0° and the resin produced kept at 0° until crystallisation was complete. The *cohumulinic acid* thus obtained (2·95 g., 88%) had, after recrystallisation successively from *cyclo*hexane, from methanol, and again from *cyclo*hexane, m. p. 79—80° (Found : C, 66·5; H, 7·85%; equiv., 248. $C_{14}H_{20}O_4$ requires C, 66·6; H, 7·9%; equiv., 252). It had pK 3·9 in aqueous ethanol. The infra-red absorption spectrum of cohumulinic acid in Nujol mull shows bands (μ) at 3·00 s, 3·89 s, 6·13 s, 6·30 s, 7·00 s, 7·31 m, 7·65 m, 7·82 s, 7·92 s, 8·02 s, 8·53 w, 8·85 w, 9·20 s, 9·75 w, 10·35 m, 10·9 w, and 11·57 w, where s = strong, m = medium, and w = weak. We are indebted to Prof. A. R. Todd and Dr. R. N. Haszeldine for this spectrum which was determined in a Perkin–Elmer double-beam instrument.

(*c*) In a similar experiment cohumulone (6·5 g.) gave a mixture of 2 : 4-dinitrophenyl-hydrazones (1·7 g.) after chromatography on alumina. A portion (11·3 mg.) of the material was separated on a benzene–formamide partition column (see below), to give *iso*butaldehyde 2 : 4-dinitrophenylhydrazone (5·7 mg. by colorimetric estimation, equiv. to an 18% yield), and acetone 2 : 4-dinitrophenylhydrazone (0·55 mg. by colorimetric estimation, equiv. to a 1·9% yield).

Dihydrocohumulinic Acid.—Cohumulinic acid (2·3 g.), when hydrogenated in methanol (150 c.c.) in the presence of Adams catalyst, absorbed 192 c.c. of hydrogen (calc. for one double bond, 207), to give a solution which after filtration and evaporation gave *dihydrocohumulinic acid*

(1·69 g., 74%), m. p. 85—87°. Recrystallisation from methanol gave prismatic needles, m. p. 91—92° (Found : C, 66·4; H, 8·8. $C_{14}H_{22}O_4$ requires C, 66·2; H, 8·7%).

Abnormal Hydrogenation of Cohumulinic Acid.—Cohumulinic acid (1·8 g.) was hydrogenated in methanol (150 c.c.) in presence of Adams platinum catalyst; 194 c.c. of hydrogen were absorbed (calc. for one double bond 170 c.c.). The solution gave a *product* as prisms, m. p. 162—163° (795 mg., 46%) after crystallisation from methanol (Found : C, 70·0; H, 10·1%; equiv., 225. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·0%; equiv., 240). Ultra-violet absorption : in acidic ethanol, max. at 250 mμ (ε 13,700); in alkaline ethanol, max. at 275 mμ (ε 21,000). The material had pK 6·0 in aqueous ethanol, and was insoluble in chloroform, water, and aqueous sodium hydrogen carbonate but soluble in aqueous sodium hydroxide and methanol. Ferric chloride in methanol gave a weak purple colour fading to brown. The material reduced alkaline permanganate and decolorised bromine in chloroform, but was unaffected by Fehling's solution or ammoniacal silver nitrate. It was recovered unchanged after 1·5 hours' boiling with N-sodium hydroxide and from attempts to prepare an oxime or semicarbazone. It consumed 1·01 molar equivalents of periodate in 3·5 hr., giving crystalline material (purple ferric chloride colour, acid to litmus, slowly gave positive Schiff test) which was hydrolysed by boiling alkali to a mixture of acids and ketones from which *iso*butyric was apparently absent (paper chromatography).

Oxidation of Dihydrocohumulinic Acid by Hypobromite.—To an ice-cooled solution of dihydrocohumulinic acid (1·67 g.) in N-sodium hydroxide solution (67 c.c.) a saturated solution of bromine (3·1 mols.) in water (103 c.c.) was added dropwise during cooling and stirring. A slight excess of bromine was reduced by sodium pyrosulphite, and the solution extracted exhaustively with ether. The extract was washed with water, dried, and evaporated, to give bromoform (995 mg., 60%), b. p. 144—145°. The alkaline oxidation solution was acidified at 0° with dilute sulphuric acid and then extracted exhaustively with ether. The extracted material was distilled at 28 cm., *iso*butyric acid (350 mg., 60%) being collected [*p*-bromophenacyl ester, m. p. and mixed m. p. 72—74°; anilide, m. p. and mixed m. p. 100—101°; R_F 0·57 on Whatman No. 1 paper in *n*-butanol–water–diethylamine (100 : 15 : 1) identical with the R_F value of *iso*butyric acid in this solvent].

Ozonolysis of Humulone.—Humulone (196 mg.) in alcohol-free chloroform was treated with ozonised oxygen for 22 min. To the solution was added powdered zinc (2 g.) and water (30 c.c.), and the mixture was kept for 30 min. and filtered. The residue was washed with water, and the combined filtrate and washings were distilled to low bulk, the distillate being collected in a solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. The hydrazones were extracted with benzene, and the extract washed with water, dried (Na_2SO_4), and concentrated. The concentrate was passed over an alumina column (Merck) in dry benzene and the coloured eluate of a single band evaporated. The residue (272 mg.) was dissolved in benzene (50 c.c.), and an aliquot part (25 c.c.) evaporated to give material which when recrystallised from ethanol had m. p. 118—120°. A further aliquot part (4 c.c.) part after evaporation to dryness was chromatographed in formamide (1 c.c.) on a " Silane "-treated kieselguhr column (42 × 1·5 cm.; 20 g. of kieselguhr, 10 ml. of benzene; cf. Howard and Tatchell, *loc. cit.*), with benzene as the stationary and formamide as the mobile phase. Two bands were eluted, each eluant solution was made up to a standard volume with formamide, and the light transmittance determined on a Spekker photoelectric absorptiometer (Ilford Filter No. 602). After extraction of the formamide solutions with benzene, washing of the benzene extract with water, drying, and evaporation, the residues were recrystallised from ethanol. In this manner the first band was identified as acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158—160°, and the second as acetone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 124°. The preparation of standard curves of acetone and acetaldehyde 2 : 4-dinitrophenylhydrazones in formamide with the Spekker photoelectric absorptiometer enabled the amounts of these compounds in the eluant solutions to be determined; it was calculated that the mixture (21·3 mg.) contained acetaldehyde 2 : 4-dinitrophenylhydrazone (2 mg., 20·6%) and acetone 2 : 4-dinitrophenylhydrazone (14 mg., 128%).

In another experiment humulone (204 mg.) was ozonised in glacial acetic acid (20 c.c.) for 22 min. and worked up as above to give a mixture of 2 : 4-dinitrophenylhydrazones (260 mg.). Separation of this mixture (21 mg.) on the partition column gave acetaldehyde 2 : 4-dinitrophenylhydrazone (3·1 mg., 30·2%) and acetone 2 : 4-dinitrophenylhydrazone (13·5 mg., 127%).

In a further experiment humulone (252 mg.) was ozonised in alcohol-free chloroform (20 c.c.) at −58° until the solution gave no colour with tetranitromethane as external indicator (23 min.). After the addition of zinc (2 g.) and water (30 c.c.) the solution was kept for 1 hr. and then

filtered. Subsequent working up gave a mixture of 2 : 4-dinitrophenylhydrazones (335 mg.), separation of which (33·5 mg.) on the partition column gave acetaldehyde 2 : 4-dinitrophenyl-hydrazone (4·5 mg., 28%) and acetone 2 : 4-dinitrophenylhydrazone (21·5 mg., 130%).

Ozonolysis of Cohumulone.—Cohumulone (290 mg.) in alcohol-free chloroform (20 c.c.) at −58° was treated with ozonised oxygen until the solution gave no colour with tetranitro-methane used as an external indicator (23 min.). After the addition of zinc (2 g.) and water (30 c.c.) the solution was kept for 3 hr., filtered, and distilled, the distillate being collected in a solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. After subsequent treatment as described for humulone a mixture of 2 : 4-dinitrophenylhydrazones (278 mg.) was obtained. The mixture was dissolved in benzene (50 c.c.), an aliquot part (5 c.c.) evaporated to dryness, and the residue (27·8 mg.) separated on the partition column into acetaldehyde 2 : 4-dinitrophenyl-hydrazone (1·75 mg., 9·4%), m. p. and mixed m. p. 160—162°, and acetone 2 : 4-dinitrophenyl-hydrazone (20·5 mg. 108%), m. p. and mixed m. p. 124°.

In a second experiment cohumulone (288 mg.) in alcohol-free chloroform was treated with ozonised oxygen at −58° for 33 min. (no colouration of tetranitromethane). After addition of zinc (2 g.) and water (30 c.c.) the solution was kept for 1 hr., then worked up in the usual way. The mixed 2 : 4-dinitrophenylhydrazones (350. mg.) thus obtained were dissolved in benzene (50 c.c.), and an aliquot part (4 c.c.) was evaporated to give a residue (28 mg.) which was dissolved in formamide and chromatographed on the partition column. The two bands on elution yielded acetaldehyde 2 : 4-dinitrophenylhydrazone (2·8 mg., 18·8%) and acetone 2 : 4-dinitro-phenylhydrazone (20·6 mg., 132%).

Ozonolysis of Humulinic Acid.—Ozonised oxygen was passed for 15 min. into a solution of humulinic acid (141 mg.) in acetic acid (20 c.c.). The solution was treated with zinc and water as usual and distilled, the distillate being collected in aqueous-ethanolic 2 : 4-dinitrophenyl-hydrazine hydrochloride. The hydrazones were extracted with benzene, and the extracts washed with water, dried (Na₂SO₄), and concentrated. The concentrate was passed over an alumina column (Merck) in dry benzene and the coloured eluate of a single band evaporated to give acetone 2 : 4-dinitrophenylhydrazone (109 mg., 86%), having m. p. and mixed m. p. 119—121° after recrystallisation from ethanol.

Ozonolysis of Cohumulinic Acid.—Cohumulinic acid (136 mg.) in acetic acid (20 c.c.) was treated with ozonised oxygen for 15 min. The solution was treated as described for humulinic acid, the single 2 : 4-dinitrophenylhydrazone band from the alumina column giving 114 mg. (89%) of acetone 2 : 4-dinitrophenylhydrazone, m. p. 117°, which had m. p. 119—121° when mixed with an authentic specimen.

Oxidation of Dihydrocohumulinic Acid with Periodate.—To dihydrocohumulinic acid (106 mg.) in ethanol (50 c.c.) was added potassium metaperiodate (117 mg., 1·22 equivs.) in water (50 c.c.). After 2 hr. 1·08 equivs. of periodate had been consumed. The solution was acidified and extracted with ether, giving an oily extract which was refluxed for 2 hr. with 2N-sodium hydroxide (30 c.c.). The hydrolysate was steam-distilled, the distillate being collected in methanolic 2 : 4-dinitrophenylhydrazine hydrochloride. The distillation residue was extracted with ether, the extracted material added to the 2 : 4-dinitrophenylhydrazine solution, and the aqueous alkaline residue reserved for later examination.

The 2 : 4-dinitrophenylhydrazones were extracted with benzene, the extracted material was passed down an alumina column (Merck), and the single main band collected. The material from this band (105 mg.) was separated on a benzene-formamide partition column into 3-methyl-butane-2-one 2 : 4-dinitrophenylhydrazone (22 mg., 20%), micro-m. p. 120—122°, and 6-methyl-heptane-2-one 2 : 4-dinitrophenylhydrazone (43·6 mg., 34%), micro-m. p. 82—83°, each un-depressed on admixture with authentic material.

The alkaline residue above was acidified and extracted with ether, and the extract washed free from inorganic acid, dried, and evaporated. Paper-chromatographic examination of the residual acids in *n*-butanol–water–diethylamine (100 : 15 : 1) gave three main acid spots, with R_F values 0·5, 0·76, and 0·89 respectively; *iso*butyric acid has R_F 0·5 in this system. Examin-ation with the solvent system *n*-butanol–water–diethylamine (25 : 25 : 1) gave four spots with R_F values 0·23, 0·48, 0·84, and 0·95 respectively.

Cohumuloquinone.—A solution of cohumulone (750 mg.) in methanol (20 c.c.) was shaken for 10 min. with 5 g. of Raney nickel to remove hydrogen sulphide remaining from the decomposition of cohumulone lead salt. The nickel was filtered off and washed with methanol (3 × 20 c.c.), a solution (5% w/v) of palladous chloride in methanol (0·2 c.c.) added to the combined filtrate and washings, and the solution hydrogenated. Uptake ceased when 134 c.c. of hydrogen had been absorbed (calc. for 3H₂, 144 c.c.). The colourless solution was

filtered and the filtrate shaken in air, 39 c.c. of oxygen being absorbed (calc. for O_2, 48 c.c.).   The purple solution was evaporated in a vacuum and the residue recrystallised twice from methanol, to give red needles (281 mg., 47%) (Found : C, 61·4; H, 7·8. $C_{15}H_{20}O_3,CH_3 \cdot OH$ requires C, 61·6; H, 7·7%).   The m. p. of the material was 72—73° but, like that of humuloquinone, the m. p. of *cohumuloquinone* was erratic.   With *o*-phenylenediamine the quinone formed a purple *azine*, m. p. 129—130°, depressed to 93—100° on admixture with humuloquinone azine of m. p. 110—111° (Found : N, 7·6. $C_{21}H_{24}O_3N_2$ requires N, 7·9%).

*iso*Cohumulinic Acid.—To an ice-cooled solution of cohumuloquinone (280 mg.) in N-sodium hydroxide (4 c.c.) and water (2 c.c.) was added slowly with stirring a saturated solution of bromine in water (15 c.c.).   The colourless solution was acidified at 0° with dilute hydrochloric acid.   The crystalline *acid* (120 mg.) was recrystallised twice from methanol, giving yellow needles, m. p. 118° (Found : C, 66·8; H, 8·3. $C_{14}H_{20}O_4$ requires C, 66·6; H, 7·9%).

Alkaline Hydrolysis of iso*Cohumulinic Acid.*—A solution of the acid (260 mg.) in freshly prepared 2N-sodium hydroxide (15 c.c.) was refluxed for 20 min. under nitrogen.   The cooled solution was filtered to remove brown gum, and the filtrate acidified at 0° with dilute hydrochloric acid.   The sticky crystals produced were recrystallised four times from benzene, giving 13 mg. of material, m. p. 102° undepressed on admixture with 3-3′-methylbutyl*cyclo*pentane-1 : 2 : 4-trione.   This mixed m. p. is not considered to be proof of the structure of the hydrolysis product.