253. *The Constitution of ψ-Santonin. Part VI. Experiments on ψ-Santonic Acid.*

By Wesley Cocker and Cyril Lipman.

Experiments performed on ψ-santonic acid are described and a tentative structure (I) is suggested for this compound.

When ψ-santonin is treated with cold concentrated hydrochloric acid, a bright yellow solution is obtained from which an acid subsequently separates (Clemo and Cocker, *J.*, 1947, 533). This dextrorotatory acid, to which the name ψ-santonic acid (I) has been given (Cocker, Cross, and Lipman, this vol., p. 959), may also be obtained in greater yield when 20% hydrochloric acid is employed, although concentrations as low as 1% initiate the formation of the acid. Cold 50% sulphuric acid is also effective.

The acid rapidly turns yellow on exposure to air in a manner reminiscent of (—)-santonin.

Analyses give the formula, $C_{15}H_{22}O_5$, which suggests the simple hydrolysis of the lactone ring of ψ-santonin ($C_{15}H_{20}O_4$), but this is not the case. ψ-Santonic acid yields a *phenylhydrazone* and a 2 : 4-*dinitrophenylhydrazone* with difficulty, and, whilst it has not been made to yield a piperonylidene derivative, it yields a *derivative* with *o*-aminobenzaldehyde which is indicative of the presence of a keto-methylene group. We have been unable to obtain a semicarbazone or an oxime, either by the usual method or by the method of Haller and La Forge (*J. Org. Chem.*, 1936, **1**, 38; cf. Dutcher and Winterstein, *J. Amer. Chem. Soc.*, 1939, **61**, 1998, and others), and this is probably due to the presence of the polarisable C:C·C:O group.

ψ-Santonic acid possesses two ethylenic groups, since (*a*) two atoms of oxygen are absorbed when the acid is titrated with perbenzoic acid and a *diepoxide* (a lactone), $C_{15}H_{20}O_6$, is produced, and (*b*) it readily absorbs two molecules of hydrogen in presence of palladised charcoal and *tetrahydro-ψ-santonic acid* results. This tetrahydro-acid was obtained as a mono-hydrated form, $C_{15}H_{24}O_4,H_2O$, m. p. 191—192°, and as a non-hydrated form, m. p. 198°; both yielded the same non-hydrated *methyl tetrahydro-ψ-santonate*, but we have been unable to obtain an ester of ψ-santonic acid itself. Tetrahydro-ψ-santonic acid yields an unhydrated *oxime* readily, and a *derivative*, $C_{22}H_{27}O_3N$, with *o*-aminobenzaldehyde. Both of these compounds are acidic, and the latter is also basic. Reduction of ψ-santonic acid in presence of Adams platinic oxide catalyst yields the alcohol, *hexahydro-ψ-santonic acid*, $C_{15}H_{26}O_4$, with uptake of six atoms of hydrogen. Acetylation of this alcohol yields an *acetate*, $C_{17}H_{26}O_4$, which is also a lactone.

ψ-Santonic acid loses two molecules of water and undergoes lactonisation when heated above its melting point, yielding the dextrorotatory *anhydro-ψ-santonic acid*, $C_{15}H_{18}O_3$, which is unaffected by cold concentrated hydrochloric acid but is converted into (+)-β-desmotropo-ψ-santonin (Cocker, Cross, and Lipman, *loc. cit.*) on warming with 50% sulphuric acid. The lactone possesses two ethylenic bonds, since on hydrogenation in presence of palladised charcoal it yields *tetrahydroanhydro-ψ-santonic acid*, $C_{15}H_{22}O_3$, the analysis being confirmed by the absorption of four atoms of hydrogen per mol. of lactone during the reduction. This tetrahydro-compound yields a 2 : 4-*dinitrophenylhydrazone*. Reduction of anhydro-ψ-santonic acid in presence of Adams platinic oxide yields the alcohol, *hexahydroanhydro-ψ-santonic acid*, $C_{15}H_{24}O_3$, with uptake of six atoms of hydrogen and reduction of the carbonyl group.

When ψ-santonin is left in contact with concentrated hydrochloric acid for long periods it yields a *compound*, $C_{15}H_{23}O_5Cl$, which is probably a hydrochloride of ψ-santonic acid.

ψ-Santonin, $C_{15}H_{20}O_4$, possesses only one ethylenic bond (see earlier publications in this series) and this is confirmed by the production of a *monoepoxide* on treatment with perbenzoic acid, whereas ψ-santonic acid, $C_{15}H_{22}O_5$, obviously possesses two such linkages. It is probable, therefore, that ψ-santonin loses a molecule of water (presumably from the C_1–C_{10} linkage) on treatment with mineral acid. The bond so formed can undergo migration. At the same time the lactone ring is hydrolysed, thus absorbing a molecule of water. It is, therefore, concluded that the ψ-santonic acid described is a monohydrated compound, $C_{15}H_{20}O_4,H_2O$, and this is confirmed by the production of a hydrated and an anhydrous tetrahydro-compound, an anhydrous *oxime* of the tetrahydro-compound, and an anhydrous ester of the latter compound.

ψ-Santonic acid shows an ultra-violet light absorption maximum at 2345 A. (log ε 4·2) and an inflexion at 3200 A. (log ε 2·3), but tetrahydro-ψ-santonic acid and its anhydro-compound has only one maximum (at 2900 A., log ε 1·7), this probably being due to an isolated keto-group. It is clear, therefore, that ψ-santonic acid is an αβ-unsaturated ketone, and the work of Woodward (*J. Amer. Chem. Soc.*, 1941, **63**, 1123), Booker, Evans, and Gillam (*J.*, 1940, 1453), and others suggests that it is a disubstituted αβ-unsaturated ketone possessing the group R•CO•CR′:CHR″ or R•CO•CH:CR′R″. This evidence conflicts with some of the chemical evidence already described. The fact that ψ-santonic acid forms a derivative with *o*-aminobenzaldehyde would seem to preclude the existence of an αβ-unsaturated keto-group, but, under the conditions of the reaction, migration of the double bond from the C_2–C_3 to the C_1–C_2 position is possible. From the ultra-violet light absorption, however, it appears that there is a substituent, presumably methyl, at either C_2 or C_3. A methyl group at C_3 is contraindicated by the formation of a derivative with *o*-aminobenzaldehyde, not only by ψ-santonic acid but also by its tetrahydro-derivative. A compound with a methyl group at C_2 would presumably give 3 : 4-dimethyl-1-naphthol by aromatisation and dehydrogenation unless migration of methyl were to take place during these processes, whereas 2 : 4-dimethyl-1-naphthol is obtained (cf. Clemo and Cocker, *loc. cit.* and Cocker, Cross, and Lipman, *loc. cit.*). The following evidence suggests that the methyl group is at the angular position, C_5, as in ψ-santonin. When tetrahydro-ψ-santonic acid is reduced under Clemmensen conditions, a gum is obtained which on dehydrogenation yields an oil, the picrate of which is identical with that of 1-methyl-7-ethylnaphthalene (Harvey, Heilbron, and Wilkinson, *J.*, 1930, 423; Clemo and Haworth, *ibid.*, 2582). Thus a methyl group is lost in the dehydrogenation, a phenomenon characteristic of compounds possessing an angular methyl group, and a double bond at C_5–C_{10} is therefore, impossible.

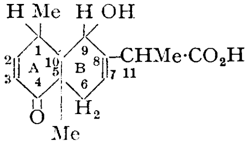
Infra-red light absorption measurements, kindly performed and interpreted by Imperial Chemical Industries, Ltd. (Billingham Division), show that ψ-santonic acid posesses absorption bands at 3500, 3430, and 3370 cm.$^{-1}$ indicating the presence of alcoholic •OH group and/or water of crystallisation in three different degrees of hydrogen bonding. A band at 3166 cm.$^{-1}$ indicates a carboxyl group involved in hydrogen bonding. A band at 1637 cm.$^{-1}$ indicates a double bond, probably conjugated with a carbonyl group, but not in a dienone system, a result in agreement with the ultra-violet light absorption data; and a band at 965 cm.$^{-1}$ probably indicates an isolated double bond. A strong band at 1696 cm.$^{-1}$ indicates the presence of a ketonic group or a carboxyl group or both.

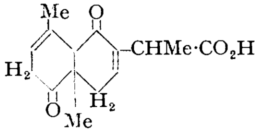
Tetrahydro-ψ-santonic acid (hydrated) possesses infra-red absorption bands indicating the presence of carbonyl and hydroxy-groups, both involved in hydrogen bonding. It possesses a strong band at 1692 cm.$^{-1}$, probably corresponding to the carboxyl group. It also possesses a broad weak band from 1620 to 1660 cm.$^{-1}$, which has not been interpreted. The oxime of this acid also possesses absorption bands indicative of the carboxyl and hydroxy-groups involved in hydrogen bonding, and a strong band at 1692 cm.$^{-1}$ attributed to the carboxyl group. A strong band at 1620 cm.$^{-1}$ is probably due to the C=N vibration, but the broad weak band shown by the parent acid is absent from the oxime.

Summarising the above evidence, it seems to us that the second double bond must be in ring B, and we believe that this double bond is that associated with the lactone ring of ψ-santonin. There are, therefore, three possible positions available for an ethylenic link, namely at C_6–C_7, C_7–C_8, and C_8–C_{11}. A double bond at either C_8–C_9 or at C_9–C_{10} would be part of an enolic system and would not be expected to behave as an olefine. A double bond at C_8–C_{11} is contra-indicated by its ready hydrogenation (cf. Cocker and Hornsby, *J.*, 1947, 1157). Since the conditions for the formation of ψ-santonic acid are mild, it is probable that the second double bond is that associated with the lactone ring in ψ-santonin which is hydrogenolysed on treatment with palladised charcoal in hydrogen. Its position at C_7–C_8 is, therefore, favoured.

In view of the above data we tentatively suggest that ψ-santonic acid is a di-unsaturated γ-hydroxy-acid of structure (I). Confirmation of this view must await the results of oxidation experiments now in hand. If ψ-santonic acid were (II), the light absorption requirements would be satisfied, but the empirical formula, $C_{15}H_{18}O_4,H_2O$, is unlikely; on this basis, ψ-santonin should have the empirical formula, $C_{15}H_{18}O_4$, and possess two double bonds for which there is no evidence.

(I.)





(II.)

When ψ-santonic acid is treated for extended periods with sodium hydroxide, it yields a *compound*, $C_{15}H_{20}O_4$, possessing a carboxyl group, which has not been further investigated, but, since during this alkaline treatment the specific rotation rises from +65° to +141° [an increase which is paralleled by the increase in rotation when (+)-β-desmotropo-ψ-santonin is epimerised by alkali to (+)-α-desmotropo-ψ-santonin (Cocker, Cross, and Lipman, *loc. cit.*)], it seems reasonable to assume that epimeric change at C_{11} has taken place. The new acid may not have been optically pure, since crystallisation to constant m. p. was very wasteful and the final material was only obtained in small yields. It should be noted that this acid is apparently unhydrated.

Both the anhydrous and the hydrated tetrahydro-ψ-santonic acid undergo lactonisation on heating with acetic anhydride, yielding *α-anhydrotetrahydro-ψ-santonic acid*, $C_{15}H_{22}O_3$, m. p. 147—148°. When heated above their melting points, the tetrahydro-ψ-santonic acids yield *β-anhydrotetrahydro-ψ-santonic acid*, m. p. 159—160°. Both forms are lævorotatory, and the α-form is converted into the β-form on shaking with hydrogen in presence of palladised charcoal. There is, however, no hydrogen uptake. Neither of the anhydro-compounds is identical with tetrahydroanhydro-ψ-santonic acid which is dextrorotatory. β-Anhydrotetrahydro-ψ-santonic acid is not identical with anhydrodihydro-ψ-santonin (Clemo and Cocker, *loc. cit.*). They possess identical melting points, which are, however, depressed on admixture, and have widely differing specific rotations

Infra-red light absorption data show that α- and β-anhydrotetrahydro-ψ-santonic acids and tetrahydroanhydro-ψ-santonic acid are structurally identical. Each has a strong band at 1698 cm.$^{-1}$ indicative of a ketonic group, and another at 1777 cm.$^{-1}$ indicative of a saturated lactone. Bands at 1622 cm.$^{-1}$ and at 832 cm.$^{-1}$, indicative of a double bond, are difficult to explain. Very weak bands at 3550 and 3380 cm.$^{-1}$, shown by all the lactones mentioned, may be overtones of those at 1777 and 1698 cm.$^{-1}$.

The inter-relations of these anhydro-compounds constitute an interesting stereochemical problem which will be investigated later, but it seems probable that these lactones differ in configuration at C_8 and C_9, the configuration at C_{11} being alike in each case. It is unfortunate that the only lævorotatory compounds so far obtained in the ψ-santonic acid series are saturated, since conversion into the yet unknown lævorotatory desmotropo-ψ-santonins is thus impossible (compare Cocker, Cross, and Lipman, *loc. cit.*).

When either α- or β-anhydrotetrahydro-ψ-santonic acid is hydrolysed, inversion of sign of rotation takes place, and a new mono-hydrated acid is obtained. It is possible that inversion at C_{11} takes place in the alkaline environment. However, when methyl tetrahydro-ψ-santonate is hydrolysed, no similar inversion of sign takes place.

It is significant that the various acids described have all been isolated in a hydrated form, whilst the lactones and ester described have been obtained only anhydrous, with the exception of the epoxide of ψ-santonic acid during the formation of which lactonisation takes place. It would appear, therefore, that in general it is the free carboxyl group which is hydrated. The infra-red data confirm that hydrogen bonding is present in the acids, but the significance of it is not clear to us.

EXPERIMENTAL.

ψ-Santonic Acid, $[\alpha]_D^{16^\circ}$ +65·4° (*c*, 1·1 in alcohol) (cf. Clemo and Cocker, *J.*, 1946, 35, who gave $[\alpha]_D^{20^\circ}$ +25·2°), can also be obtained (2 g.) by stirring ψ-santonin (3 g.) for 2—3 hours with sulphuric acid (5 c.c.) and water (10 c.c.), or by shaking ψ-santonin for 24 hours with 20% hydrochloric acid. By treatment with concentrated hydrochloric acid for 12 hours, ψ-santonin yields also a *chloro*-compound which crystallises from dilute acetic acid as prisms, m. p. 289—290° (Found: C, 56·2; H, 6·9. $C_{15}H_{23}O_5Cl$ requires C, 56·6; H, 7·2%). *ψ-Santonic acid 2 : 4-dinitrophenylhydrazone* has m. p. 193—194° (Found: C, 55·0; H, 5·6. $C_{21}H_{26}O_8N_4$ requires C, 54·5; H, 5·6%). *Anhydro-ψ-santonic acid phenylhydrazone*, formed with phenylhydrazine in boiling acetic acid, separated from benzene in small orange needles, m. p. 160° (Found: C, 75·2; H, 7·0. $C_{21}H_{24}O_2N_2$ requires C, 75·0; H, 7·1%).

ψ-Santonic Acid Diepoxide.—ψ-Santonic acid (1 g.) in chloroform (50 c.c.) was set aside for 15 days at 0° with perbenzoic acid in chloroform (20 c.c.; 0·9N.). The solid *diepoxide* produced was washed with chloroform and then crystallised from alcohol in prisms, m. p. 265—266° after softening at 252°, $[\alpha]_D^{12^\circ}$ −45·9° (*c*, 0·25 in alcohol) (Found: C, 60·7; H, 6·7. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·8%). In a quantitative experiment 1·8 double bonds per mol. were found.

Condensation of ψ-Santonic Acid with o-*Aminobenzaldehyde.*—This was performed as described for ψ-santonin (*loc. cit.*). The gummy *product* which was first obtained gave a solid, m. p. 138—140°, on rubbing with light petroleum (Found: N, 3·5. $C_{22}H_{25}O_4N$ requires N, 3·8%).

Tetrahydro-ψ-santonic Acid (III).—ψ-Santonic acid (1 g.) in acetic acid (25 c.c.) was shaken in hydrogen for 11 hours with palladised charcoal (0·1 g.). The *tetrahydro-acid* separated from dilute alcohol in needles (0·4 g.), m. p. 197—198°, $[\alpha]_D^{23^\circ}$ +52° (*c*, 0·9 in alcohol) (Found: C, 67·1; H, 8·9. $C_{15}H_{24}O_4$ requires C, 67·1; H, 8·9%). In a quantitative experiment two double bonds per mol. were found. The *oxime* (needles from alcohol) had m. p. 230° (decomp.) (Found: C, 63·8; H, 8·8. $C_{15}H_{25}O_4N$ requires C, 63·6; H, 8·8%). A *monohydrate* consisted of prisms, m. p. 190—191°, $[\alpha]_D^{14^\circ}$ +32·4° (*c*, 0·9 in alcohol) (Found: C, 63·3; H, 9·0. $C_{15}H_{24}O_4,H_2O$ requires C, 62·9; H, 9·0%).

Methyl tetrahydro-ψ-santonate (IV) was obtained when the acid (III) (0·2 g.) was heated under reflux in methyl alcohol with methyl iodide (4 c.c.) and anhydrous potassium carbonate (1·0 g.). The *ester* separated from light petroleum (b. p. 60—80°) in needles (50 mg.), m. p. 68—69° (Found: C, 68·5; H, 8·7. $C_{16}H_{26}O_4$ requires C, 68·1; H, 9·2%).

Condensation of Tetrahydro-ψ-santonic Acid with o-*Aminobenzaldehyde.*—This gave a *product* which crystallised from alcohol in needles, m. p. 212—213° (Found: C, 74·9; H, 7·4. $C_{22}H_{27}O_3N$ requires C, 74·8; H, 7·6%).

Anhydro-ψ-santonic Acid (V).—ψ-Santonic acid (0·6 g.) was heated at 200° for 10 minutes; after being cooled, the product was agitated with 10% sodium carbonate. The residual *lactone* crystallised from alcohol as pale yellow prisms (0·5 g.), m. p. 191—192°, $[\alpha]_D^{19^\circ}$ +110° (*c*, 1·1 in chloroform) (Found: C, 72·6; H, 7·3. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·3%).

Tetrahydroanhydro-ψ-santonic Acid (VI).—The lactone (V) (0·2 g.) in acetic acid (10 c.c.) was shaken in hydrogen for 9 hours with palladised charcoal (0·3 g.). The resulting gummy product solidified on stirring with alcohol, from which solvent the required *lactone* was obtained (0·1 g.) as needles, m. p. 119—120°, $[\alpha]_D^{19^\circ}$ +10·2° (*c*, 1·0 in alcohol) (Found: C, 71·9; H, 8·8. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%). In a quantitative experiment, 4 atoms of hydrogen per molecule were absorbed. The 2 : 4-*dinitrophenylhydrazone* of *tetrahydroanhydro-ψ-santonic acid* separated from alcohol as orange needles, m. p. 220—221° (decomp.) (Found: C, 58·5; H, 5·9. $C_{21}H_{26}O_6N_4$ requires C, 58·6; H, 6·0%).

Hexahydroanhydro-ψ-santonic Acid (VII).—Anhydro-ψ-santonic acid (V) (0·5 g.) in acetic acid (15 c.c.) was shaken in hydrogen for 20 hours with platinic oxide (0·1 g.). The *lactone* produced crystallised from dilute alcohol as long needles (0·1 g.), m. p. 150—152° (Found: C, 71·9; H, 8·7. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·5%). In a quantitative experiment 6 atoms of hydrogen per molecule were absorbed.

Hexahydro-ψ-santonic Acid.—ψ-Santonic acid (1·0 g.) in glacial acetic acid (15 c.c.), when shaken with platinic oxide (0·5 g.) in an atmosphere of hydrogen for 12 hours, gave the *hexahydro-acid*, which crystallised from dilute alcohol as long, glistening needles, m. p. 185° (Found: C, 63·7; H, 9·4. $C_{15}H_{26}O_4,H_2O$ requires C, 62·5; H, 9·6%). Its *acetate*, first obtained as a gum, eventually solidified and crystallised from dilute alcohol as needles, m. p. 120—121° (Found : C, 69·2 ; H, 8·4. $C_{17}H_{26}O_4$ requires C, 69·4; H, 8·6%). This compound was a lactone. In a quantitative experiment, 5·4 atoms of hydrogen per molecule were absorbed.

α-Anhydrotetrahydro-ψ-santonic Acid.—When tetrahydro-ψ-santonic acid, m. p. 197—198°, was heated with a mixture of acetic anhydride and sodium acetate, it yielded solid *α-anhydrotetrahydro-ψ-santonic acid*, which crystallised from dilute acetic acid as needles, m. p. 147—148°, $[\alpha]_D^{21^\circ}$ −133°, (*c*, 0·4 in alcohol) (Found : C, 72·3, 72·4; H, 8·2, 8·5. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol as orange needles, m. p. 210° (decomp.) (Found : C, 58·3; H, 6·0. $C_{21}H_{26}O_6N_4$ requires C, 58·5; H, 6·0%). This anhydro-acid (0·2 g.) was shaken in acetic acid (10 c.c.) with palladised charcoal (0·1 g.) in hydrogen. Crystallisation of the product from dilute alcohol yielded colourless needles (0·1 g.), m. p. 159—160°, $[\alpha]_D^{20^\circ}$ −37·5° (c, 0·4 in alcohol) (Found : C, 72·0; H, 8·8. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%), identical with *β-anhydrotetrahydro-ψ-santonic acid* (0·1 g.; m. p. 159—160°. Found : C, 71·8; H, 8·8%) obtained when tetrahydro-ψ-santonic acid (0·2 g.) was heated at 195—200° for 10 minutes.

Hydrolysis of α- and β-Anhydrotetrahydro-ψ-santonic Acid.—α-Anhydrotetrahydro-ψ-santonic acid (0·06 g.) was heated with 2N-sodium hydroxide (4 c.c.) until complete solution was effected. The cooled solution was acidified at 0° with concentrated hydrochloric acid. The resultant *acid* crystallised from dilute alcohol as long, silky needles, m. p. 205—206°, $[\alpha]_D^{19^\circ}$ +103·3° (*c*, 0·272 in alcohol) (Found : C, 62·9; H, 8·9. $C_{15}H_{24}O_4,H_2O$ requires C, 62·9; H, 9·1%). It dissolved in sodium carbonate solution with effervescence. β-Anhydrotetrahydro-ψ-santonic acid yielded the same acid.

Action of Sodium Hydroxide on ψ-Santonic Acid.—ψ-Santonic acid (0·7 g.) in sodium hydroxide (6 c.c., 8%) was set aside at room temperature for one week. The filtered solution was acidified and gave a solid (0·55 g.), m. p. 218—220°. After many crystallisations from dilute acetic acid, the *acid* was deposited as minute needles, m. p. 254°, $[\alpha]_D^{13^\circ}$ +141° (*c*, 0·8 in acetic acid) (Found : C, 67·2; H, 7·7; equiv., 250. $C_{15}H_{20}O_4$ requires C, 67·4; H, 8·0%; equiv., 264).

Deoxytetrahydro-ψ-santonic Acid.—The tetrahydro-compound (III) (2·8 g.) was heated under reflux with amalgamated zinc (15 g.), concentrated hydrochloric acid (30 c.c.), and toluene (30 c.c.) for 24 hours. On being rubbed with ether, the glassy product gave a white solid (0·35 g.), which crystallised from dilute alcohol as long needles, m. p. 166—167°, $[\alpha]_D^{18^\circ}$ −37·3° (*c*, 0·92 in chloroform) (Found : C, 72·1; H, 8·4. $C_{15}H_{22}O_3$ requires C, 72·0; H, 8·8%). This *compound* has not been further investigated. Its 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol as yellow needles, m. p. 234—235° (Found : C, 58·0; H, 5·9. $C_{21}H_{26}O_6N_4$ requires C, 58·1; H, 6·0%). The gummy residue from the white solid was heated at 280—340° for 40 hours with an excess of selenium (1 g.), yielding an oil (0·2 g.) which was distilled from sodium, b. p. 110—115°/2—3 mm. Its picrate crystallised from alcohol as orange needles, m. p. 91—92°, which did not depress the m. p. of the picrate of authentic 1-methyl-7-ethylnaphthalene, m. p. 94° (Ruzicka and Eichenberger, *Helv. Chim. Acta*, 1930, **13**, 117).

Epoxide of ψ-Santonin. Titration of ψ-Santonin with Perbenzoic Acid.—ψ-Santonin (1·001 g.) in chloroform (10 c.c.) was set aside at 0° for 15 days with a solution of perbenzoic acid (20 c.c.; 0·9N.). Titration of the excess of perbenzoic acid in an aliquot proportion showed the presence of one double bond per molecule. The remaining solution was washed with sodium bicarbonate and evaporated to dryness; a gum was obtained which solidified on grinding with ether. The *epoxide* (0·85 g., m. p. 135°) crystallised from a mixture of ethyl acetate and light petroleum as rosettes of needles, m. p. 145·5—146·5° (Found : C, 64·4; H, 7·2. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·1%). It yielded a 2 : 4-dinitrophenylhydrazone, m. p. 238—240°.

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