[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NATIONAL INSTITUTE OF HEALTH]

Santonin Analogs. V. Desmotropodihydroalantolactone from Dihydro-alantolactone and -isoalantolactone[1]

BY SATOSHI NAKAZAWA

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A new isomeric dihydroalantolactone having a double bond in its C_{4-10}-position has been obtained. This was converted into a dienone which gave desmotropodihydroalantolactone by mild acid treatment. From the observed tendency of the desmotropo compound to be converted to a stable C_{11}-isomer, the stereochemical arrangement of C_{11}-methyl group in the original dihydroalantolactone was deduced.

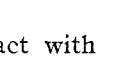
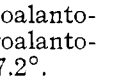
The former structure of tetrahydroalantolactone given by Ruzicka[2] has been revised on the basis of recent reinvestigations by Tsuda, *et al.*,[3] Šorm, *et al.*,[4,5] Tanabe[6,7] and Cocker, *et al.*[8] to (I).

In a previous paper of this series[9] the author reported on the purification of both dihydroalantolactone (II) and dihydroisoalantolactone (III), which were isolated in pure state and in good yield. Using these materials, a further research on the conformation of the C_{11}-methyl of tetrahydroalantolactone which remained unsettled was undertaken and the results are now reported.

Hydrogen bromide was allowed to react with cooling on an alcoholic solution of dihydroalantolactone (II) to give 4-bromotetrahydroalantolactone (IV), m.p. 120–121° dec., $[\alpha]^{18}D$ +7.2°.

Compound IV was also obtainable from dihydroisoalantolactone (III) by similar treatment. Thus the position of bromine substituted is at C_4. Contrary to the above, when hydrobromination was performed at room temperature both dihydroalantolactone (II) and dihydroisoalantolactone (III) gave an isomeric bromide V, m.p. 189–191° dec., $[\alpha]^{16}D$ −67.6°. As V is more stable than IV, the bromine at the C_4-position of these two isomers appears to be equatorial (α) and axial (β), respectively. However, by catalytic hydrogenation with palladized calcium carbonate, IV was converted into a tetrahydroalantolactone which is known to have the C_4-methyl group in the β-orientation. And by similar treatment, V gave an isomeric tetrahydroalantolactone (VII), m.p. 120–121°, $[\alpha]^{17}D$ − 22.8°, having the C_4-methyl group in the α-orientation, which was already reported by Iwai[10] and Tanabe[7] and named β-tetrahydroalantolactone.

When the bromide IV was boiled with γ-collidine, three dehydrobrominated products, dihydroalantolactone (II), dihydroisoalantolactone (III) and a new isomeric dihydroalantolactone IX, were obtained and separated from each other with yields of *ca.* 20, 30 and 20%, respectively. The new isomeric dihydroalantolactone (IX) was oxidized with selenium dioxide to give a monoenonic compound (X), m.p. 99–101°, $[\alpha]^{17}D$ + 99.8°, λ_{max}^{EtOH} 246 mμ (log ε 4.17), and by further heating with the same oxidation agent in glacial acetic acid X was converted into a dienonic compound (XI), m.p. 176–178°, $[\alpha]^{17}D$ − 122.8°.

This product XI showed specific absorptions for both dienone structure and γ-lactone [λ_{max}^{EtOH} 242 mμ (log ε 3.98), $\nu_{max}^{CHCl_3}$ 1660 (), 1760 cm.$^{-1}$ (*cis*-lactonic carbonyl)[11,12]] comparable with those for *l*-α-santonin, which has λ_{max}^{EtOH} 241 mμ (log ε 4.12), and $\nu_{max}^{CHCl_3}$ 1670 (), 1785 cm.$^{-1}$ (*trans*-lactonic carbonyl). However XI showed no coloration with sodium methoxide as in the case of santonin.

The optical rotatory dispersion curves for both X and XI were measured by the courtesy of Dr. Carl Djerassi and the curves were typical of those of Δ^4-3-ketosteroids and $\Delta^{1,4}$-3-ketosteroids, respectively. Further, from the analogy of a similar curve for α-cyperone, the side chains at the C_6-positions of X and XI are in the β-orientation[13] (Fig. 1).

The dienonic compound XI was converted into a desmotropo compound (XII), m.p. 217–218°, $[\alpha]^{17}D$ + 28.0°, by dienone–phenol rearrangement with 55% sulfuric acid. By further heating of the desmotropo compound XII with potassium carbonate in xylene, another isomeric desmotropo compound (XIII), m.p. 193–195°, $[\alpha]^{16}D$ + 145.9°, was obtained. These dienonic and two desmotropo compounds, XI, XII and XIII, were different from the corresponding derivatives of santonin and by reductive treatment with zinc dust–acetic acid of the former compounds no cleavage of lactonic linkage was observed as in the case of similar derivatives having *cis* fused lactonic structures in the santonin series.

In studies of the structure of desmotropo-ψ-santonin, Dauben[14] has pointed out that this type of reductive cleavage of lactonic linkage with zinc dust–acetic acid is observable only for compounds having a benzylic hydroxyl structure as in the case of desmotroposantonin.

(1) Paper IV in this series, T. Ukita and S. Nakazawa, THIS JOURNAL, **82**, 2224 (1960).

(2) L. Ruzicka, P. Pieth, Th. Reichstein and L. Ehmann, *Helv. Chim. Acta*, **16**, 268 (1933).

(3) K. Tsuda, K. Tanabe, I. Iwai and K. Funakoshi, THIS JOURNAL, **79**, 5721 (1957).

(4) Ö. Kovács, V. Herout, M. Horák and F. Šorm, *Collection Czechoslov. Chem. Commun.*, **21**, 225 (1956).

(5) V. Benešová, V. Sýkora, V. Herout and F. Šorm, *Chemistry & Industry*, 363 (1958).

(6) K. Tanabe, *Pharm. Bull.*, **6**, 214 (1958).

(7) K. Tanabe, *ibid.*, **6**, 218 (1958).

(8) W. Cocker and T. B. H. McMurry, *Proc. Chem. Soc.*, 147 (1958).

(9) T. Ukita, R. Matsuda and S. Nakazawa, *Yakugaku Zasshi*, **72**, 796 (1952).

(10) H. Matsumura, I. Iwai and E. Ohki, *Yakugaku Zasshi*, **74**, 738 (1954).

(11) J. H. Brewster and C. H. Kucera, THIS JOURNAL, **77**, 4564 (1955).

(12) T. Kanzawa, H. Kamio, M. Sumi and M. Nishikawa, *ibid.*, **80**, 3705 (1958).

(13) C. Djerassi, R. Riniker and B. Riniker, *ibid.*, **78**, 6362 (1956).

(14) W. G. Dauben, P. D. Hance and W. K. Hayes, *ibid.*, **77**, 4609 (1955).

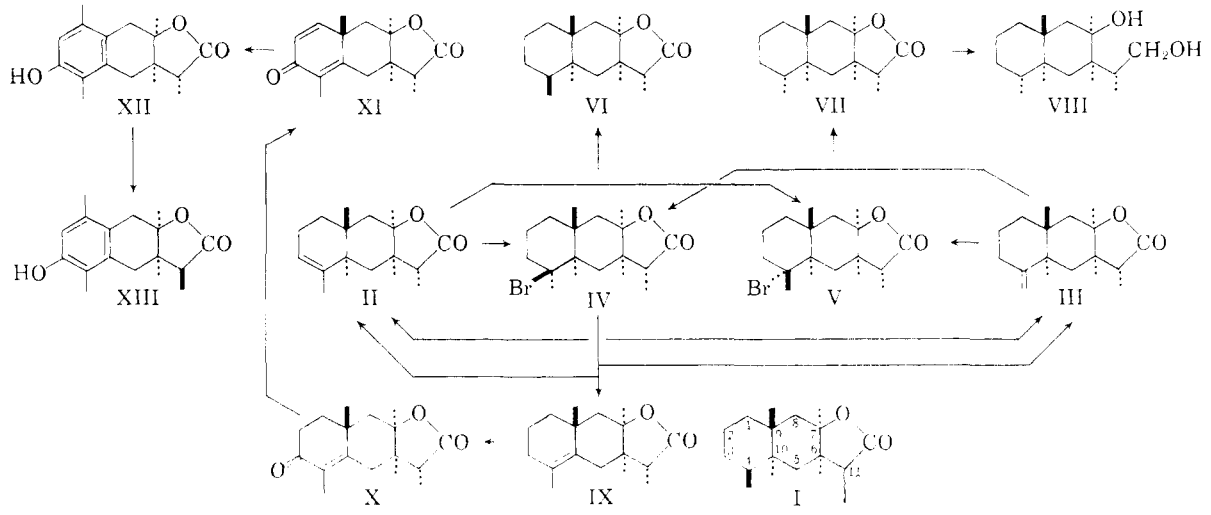


Chart.

Thus the failure of this reaction for both XI and XII again gives evidence that the hydroxyl group involved in lactonic linkage in alantolactone must not be at the C_5-position as represented by Tsuda, *et al.*[3]

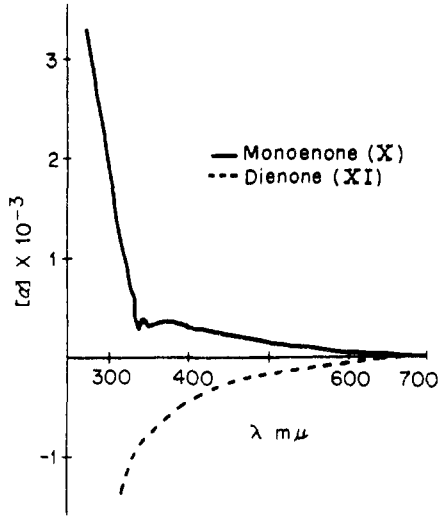


Fig. 1.

Both infrared absorption spectra and optical rotatory dispersion curves show that the dienonic XI and the desmotropo compounds (XII), have *cis* fused lactone rings, and because all the steps in the course of reactions from the original alantolactone to XI and XII involve no reaction resulting in any conformational change at C_6, C_7, C_{11}, the dihydroalantolactone (II) and dihydroisoalantolactone (III) must also contain a *cis* fused lactone ring.

As XIII was obtained by a treatment of XII with potasssium carbonate in boiling xylene, conditions which are usually used for isomerization of the C_{11}-methyl in the desmotroposantonin series,[15,16] in desmotropodihydroalantolactone (XIII) the methyl group must be in a more stable arrangement than that in the desmotropo compound XII, which retains the original configuration of the methyl group in the dihydroalantolactones II and III.

Woodward and Yates,[17] Corey[18] and Cocker[19] have suggested the β-orientation for the C_{11}-methyl in the santonin series. But from the result of recent work on the conformation of the C_{11}-methyl in the santonin series, applying Prelog's method[20] for 11-noreusantonan-11-ol, contrary to the above workers, Abe and Miki[21] have concluded that the C_{11}-methyl has the α-orientation and the methyl group is more stable in the *trans* fused lactone when the methyl and C_6–H are in the *cis* configuration; in the *cis* fused lactone the methyl is more stable when it is in *trans* configuration with C_6–H. Further results were confirmed by another series of reactions by Yanagita, *et al.*[22]

According to the latter authors, because desmotropodihydroalantolactone (XIII) is more stable than XII and these have *cis* fused lactones, the C_{11}–methyl in XII should be situated in the *cis* configuration to C_6–H. Thus the total conformational structure for tetrahydroalantolactone is to be represented by VI.

Experimental[23]

Hydrobromination of Dihydroalantolactone (II) to 4β-Bromotetrahydroalantolactone (IV) and 4α-Bromotetrahydroalantolactone (V).—(a) A suspension of 1 g. of dihydroalantolactone (II) in 10 ml. of absolute ethanol was saturated with hydrogen bromide with ice cooling, and the solvent was evaporated under reduced pressure to give 1.35 g. of colored oily product. On standing, after the addition of a small quantity of ether and petroleum ether, crystals separated and were collected and washed with a small quantity of the same solvent. Recrystallization from petroleum ether gave colorless silky needles of IV, m.p. 120–121° dec., $[\alpha]^{13}D$

(15) W. Cocker, B. E. Cross and C. Lipman, *J. Chem. Soc.*, 955 (1949).

(16) W. Cocker and T. B. H. McMurry, *ibid.*, 4430 (1955).

(17) R. B. Woodward and P. Yates, *Chemistry & Industry*, 1391 (1954).

(18) E. J. Corey, THIS JOURNAL, **77**, 1044 (1955).

(19) W. Cocker and T. B. H. McMurry, *Chemistry & Industry*, 1199 (1954).

(20) V. Prelog, *Helv. Chim. Acta*, **36**, 308, 320, 325 (1953).

(21) T. Miki, *Yakugaku Zasshi*, **75**, 416 (1955); Y. Abe, T. Miki and M. Sumi, 11th Annual Meeting of the Pharmaceutical Society of Japan, at Nagoya (Apr. 9, 1958).

(22) M. Yanagita and H. Ogura, Monthly Meeting of Pharmaceutical Society of Japan, at Tokyo (Sept. 29, 1958).

(23) All melting points are uncorrected.

+7.2° (*c* 2.5, ethanol). *Anal.* Calcd. for $C_{15}H_{23}O_2Br$: C, 57.14; H, 7.30. Found: C, 57.32; H, 7.31.

(b) A similar reaction was performed at room temperature to yield 1.35 g. of crystalline product. Recrystallization from petroleum ether gave colorless needles of V, m.p. 189–191° dec., $[\alpha]^{16}D$ − 67.6° (*c* 0.5, ethanol). *Anal.* Calcd. for $C_{15}H_{23}O_2Br$: C, 57.14; H, 7.30. Found: C, 57.39; H, 7.07.

Hydrobromination of Dihydroisoalantolactone (III) to 4β-Bromotetrahydroalantolactone (IV) and 4α-Bromotetrahydroalantolactone (V).—Compounds IV and V were obtained also from III by a similar reaction.

Catalytic Hydrogenation of 4β-Bromotetrahydroalantolactone (IV) and 4α-Bromotetrahydroalantolactone (V) to Tetrahydroalantolactone (VI) and β-Tetrahydroalantolactone (VII), Respectively.—(a) A solution of 0.32 g. of 4β-bromotetrahydroalantolactone (IV) in 30 ml. of ethanol was poured into a suspension of palladized calcium carbonate catalyst prepared from 0.14 g. of 6% palladized calcium carbonate in 15 ml. of ethanol. The mixture was shaken in a hydrogen atmosphere, 24 ml. of hydrogen was consumed during 10 hours at 15° (761 mm.) (calcd. for one mole, 24.6 ml.). After treatment of the mixture in the usual manner 0.24 g. of crude product was obtained. Recrystallization from ethanol gave colorless needles, m.p. 142–144°. This product was identified with tetrahydroalantolactone (VI).

(b) A solution of 0.32 g. of 4α-bromotetrahydroalantolactone (V) in 30 ml. of ethanol was catalytically hydrogenated with palladized calcium carbonate as above; 26.0 ml. of hydrogen was consumed during 5 hours at 24.5° (753.5 mm.) (calcd. for one mole, 25.8 ml.). From the reaction mixture 0.24 g. of crude product was obtained. Recrystallization from petroleum ether gave colorless needles of VII, m.p. 120–121°, $[\alpha]^{17}D$ −22.8° (*c* 1.0, ethanol). *Anal.* Calcd. for $C_{15}H_{24}O_2$: C, 75.27; H, 10.17. Found: C, 76.27; H, 10.27.

This product was identified with β-tetrahydroalantolactone (VII).

Reduction of β-Tetrahydroalantolactone (VII) with Lithium Aluminum Hydride to the Glycol VIII.—A solution of 0.2 g. of β-tetrahydroalantolactone (VII) was added dropwise to a solution of 0.08 g. of lithium aluminum hydride in 20 ml. of ether at room temperature with stirring. After additional stirring for 2 hours, the mixture was treated in the usual manner to yield 0.2 g. of crude crystalline product. Recrystallization from petroletum ether gave colorless needles of VIII, m.p. 121–122°, $[\alpha]^{17}D$ −31.9° (*c* 1.0, ethanol). *Anal.* Calcd. for $C_{15}H_{28}O_2$: C, 75.00; H, 11.66. Found: C, 75.09; H, 11.83.

Dehydrobromination of 4β-Bromotetrahydroalantolactone (IV) to Dihydroalantolactone (II), Dihydroisoalantolactone (III) and New Isomeric Dihydroalantolactone (IX).—A solution of 1.10 g. of 4β-bromotetrahydroalantolactone (IV) in 20 ml. of γ-collidine was refluxed for 30 minutes, and the mixture was poured into 100 ml. of ice-water and the mixture was treated by the usual manner to obtain 0.87 g. of crude product. This product was recrystallized several times from ethanol to remove III, which has the least solubility in this solvent.

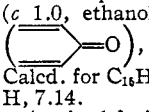
The filtrates obtained after removal of III were combined and the solvent was evaporated to dryness. The residue was recrystallized with dilute methanol to give crude II which was purified by further recrystallization from methanol.

From the filtrate of the latter recrystallization, the solvent was removed and the dry residue was again recrystallized from petroleum ether to give the crude IX which was purified by further recrystallization from the same solvent to constant melting point of 63–65°, $[\alpha]^{25}D$ +16.2° (*c* 0.8, ethanol). *Anal.* Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.12; H, 9.54.

The three olefins III, II and IX thus obtained showed constant melting points and specific rotations on further recrystallization and their yields were 0.25, 0.18 and 0.17 g., respectively.

Dehydrobromination of 4α-Bromotetrahydroalantolactone (V) to Dihydroalantolactone (II) and Dihydroisoalantolactone (III).—A solution of 1.0 g. of 4α-bromotetrahydroalantolactone (V) in 20 ml. of γ-collidine was treated by the same manner as described above to give 0.24 g. of III, and 0.15 g. of II.

Oxidation of the New Isomeric Dihydroalantolactone IX with Selenium Dioxide to the Monoenonic Compound X.—To a gently refluxing solution of 0.47 g. of IX in 20 ml. of ethanol was added dropwise a solution of 0.22 g. of selenium dioxide in 10 ml. of the same solvent with stirring. After stirring for 5 hours, the selenium which had separated was removed by filtration, the solvent was evaporated under reduced pressure, and the residue was diluted with ethyl acetate. The ethyl acetate solution was washed with 5% sodium carbonate solution and water and dried over anhydrous sodium sulfate. The residue obtained after evaporation of the solvent was treated with Girard P reagent to isolate 0.32 g. of oily ketonic product, which crystallized on standing. Recrystallization from ethyl acetate–petroleum ether gave colorless plates of X, m.p. 99–101°, $[\alpha]^{17}D$ +99.8° (*c* 1.0, ethanol), λ_{max}^{EtOH} 246 mμ (log ε 4.17). *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 72.58; H, 8.06. Found: C, 72.22; H, 8.28.

Dehydrogenation of the Monoenonic Compound X by Selenium Dioxide to the Dienonic Compound XI.—To a solution of 0.49 g. of the monoenonic compound X in 5 ml. of glacial acetic acid was added 0.25 g. of selenium dioxide in 1 ml. of water. The mixture was refluxed gently for 45 minutes. After removal of selenium by filtration, the solvent was evaporated under reduced pressure, and the residue was diluted with benzene. The benzene solution was washed with 5% sodium carbonate solution and water, dried over anhydrous sodium sulfate and evaporated. On distillation of the residual oil, 0.2 g. of crystalline distillate contaminated with a small quantity of selenium was obtained. This was redissolved in benzene and well washed with 5% sodium hydroxide solution, the benzene layer dried and evaporated. Distillation of the residue gave 0.13 g. of crystalline product, which was decolorized by charcoal in ethyl acetate. Recrystallization from ethyl acetate–petroleum ether gave colorless prisms of XI, m.p. 176–178°, $[\alpha]^{17}D$ − 122.8° (*c* 1.0, ethanol), λ_{max}^{EtOH} 242 mμ (log ε 3.98); $\nu_{max}^{CHCl_3}$ 1660  , 1760 cm.$^{-1}$ (*cis* lactonic carbonyl). *Anal.* Calcd. for $C_{15}H_{18}O_2$: C, 73.17; H, 7.32. Found: C, 72.77; H, 7.14.

A mixed fusion of this dienonic compound (XI) with *l*-α-santonin showed depression, (m.p. 129–137°). This product showed no color reaction with sodium methoxide, which colors *l*-α-santonin pink.

Reduction of the Dienonic Compound XI by Zinc Dust.—A solution of 60 mg. of XI in 5 ml. of methanol containing 0.1 g. of zinc dust and 5 drops of glacial acetic acid was refluxed on a water-bath for 1 hour. The mixture was treated in the usual manner, but gave no acidic product except 50 mg. of starting material.

Dienone-Phenol Rearrangement of the Dienonic Compound XI to Desmotropodihydroalantolactone XII.—To 80 mg. of XI was added 2 ml. of 55% sulfuric acid and the mixture was kept at 50° for 20 hours. The mixture then was diluted with 20 ml. of ice-water, and extracted with ethyl acetate. The ethyl acetate solution was washed with 5% sodium carbonate and again extracted with 5% sodium hydroxide solution. The latter alkaline solution was treated as usual to obtain 70 mg. of phenolic crystalline compound. Recrystallization from ethyl acetate–petroleum ether gave colorless prisms of XII, m.p. 217–218°, $[\alpha]^{17}D$ +28.0° (*c* 0.99, ethanol), λ_{min}^{EtOH} 251 mμ (log ε 2.36), λ_{max}^{EtOH} 284 mμ (log ε 3.34), $\nu_{max}^{CHCl_3}$ 1760 cm.$^{-1}$ (*cis* lactonic carbonyl).

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 73.17; H, 7.32. Found: C, 73.52; H, 7.32.

Reduction of the Desmotropo Compound XII with Zinc Dust.—A solution of 30 mg. of XII in 3 ml. of methanol was refluxed with 0.1 g. of zinc dust and 3 drops of glacial acetic acid on a water-bath for 1 hour. The mixture, treated in the usual manner, gave no acidic product but 20 mg. of starting material.

Isomerization of the Desmotropo Compound XII to the Isomeric Desmotropo Compound XIII.—Compound XII (40 mg.), 5 ml. of xylene and 100 mg. of dry potassium carbonate was boiled for 24 hours; 30 mg. of phenolic compound was isolated by the procedure of Cocker.[15] Successive recrystallization from ethyl acetate–petroleum ether and aqueous methanol gave colorless prisms of XIII, m.p. 193–195°, $[\alpha]^{16}D$ +145.9° (*c* 0.3, ethanol), λ_{min}^{EtOH} 252 mμ (log ε 2.36), λ_{max}^{EtOH} 285 mμ (log ε 3.22). *Anal.* Calcd. for $C_{15}H_{18}O_3$: C, 73.17; H, 7.32. Found: C, 73.30; H, 7.46.

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ment of Prof. T. Ukita, at University of Tokyo. The author is also indebted to Dr. D. Mizuno, the Chief of Department of Chemistry, National Institute of Health, Prof. K. Tsuda, University of Tokyo, and Prof. M. Yanagita, Keio-Gijuku University, for their interest. Thanks are also due to Prof. Carl Djerassi, Wayne State University, for his kindness in obtaining optical rotatory dispersion curves of the new derivatives and to the Takeda Pharmaceutical Industries, Ltd., for the measurement of infrared spectra and to Misses R. Ohta, E. Kondo, S. Hara and Mr. B. Kurihara for performing the microanalyses.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

The Stereochemistry of ψ-Santonin[1]

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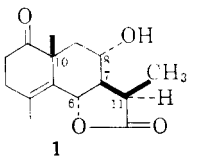
Previous studies pertaining to the stereochemistry of ψ-santonin are discussed. In the present work, further evidence for the *trans* relationship between the C-7 side-chain and the C-8 hydroxyl group was found by the preparation of 8-epi-ψ-santonin (**10**) and a study of its reactions. The *cis* nature of the 6,12-lactone was established: (a) by evaluation of the steric demands of the reactions employed to resynthesize ψ-santonin from **4**, (b) by evaluation of the steric requirements needed for hydrogenolysis of an allylic lactone, and (c) by establishment of the structure of iso-ψ-santonin as an 11-iso derivative (**14**). The stereochemistry of the C-11 methyl group was shown to be the same as in (−)-α-santonin by a study of the stability of the isomeric desmotropo-ψ-santonins. Further, it was found that (+)-α-isodesmotropo-ψ-santonin possessed structure **35a** rather than **32** previously assigned. The stereochemistry of ψ-santonin is represented by **43**.

ψ-Santonin is a sesquiterpene lactone isolated from *Artemisia* and on the basis of a series of chemical transformations was assigned the gross structure **1**.[3-6] By consideration of the steric demands of certain of the transformations, Cocker and his coworkers[7] suggested the steric representation shown in **1**.[8] During the course of our continuing investigation of the chemistry of the interesting material,



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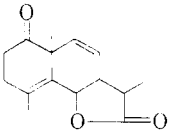
results have been obtained which permit an unequivocal assignment of configuration to all of the asymmetric centers and necessitate a minor revision of formula **1**. The importance of the stereochemistry of this material stems from the fact that it has served as a relay in relating the sesquiterpenic lactones (−)-α-santonin and artemisin[9] to alantolactone[10,11] and costol[12,13] which, in turn, have been related to β-selinene[14,15] whose absolute configuration is known. As a result of these transformations, the absolute stereochemistry of the side-chain at C-7 and the angular methyl group at C-10 of ψ-santonin is known with certainty.

The configuration of the C-8 hydroxyl group as *trans* to the C-7 side-chain can be assigned on the basis of various results. First, the dehydration of ψ-santonin is difficult, suggesting an equatorial conformation and hence a *trans* relationship to the C-7 side-chain which is equatorial. Also, this dehydration does not involve the usually preferred tertiary hydrogen on C-7, but a 8,9-ene (**2**) is formed.[3] Second, the lactone **3**, derivable from ψ-santonin,[10] is identical with a tetrahydroalantolacetone isomer which is known to possess a *trans*-lactone grouping.[11] Third, by application of the lactone rule of



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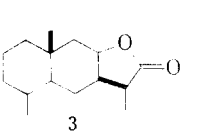

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Klyne[16] concerning the absolute configuration of the potential hydroxyl group it can be concluded[17] that the oxygen function possesses an opposite absolute configuration to that of C-7 side-chain and C-10 methyl group. Further evidence of the *trans* relationship now has been obtained. It has been reported previously[4] when ψ-santonin (**1**) is hydrogenated that hydrogenolysis of the allylic lactone with concomitant migration of the double bond occurs to yield the hydroxy acid **4**. This acid shows no tendency to lactonize spontaneously, and to obtain the lactone **5** it must be treated with acetic anhydride. When the tosylate of ψ-santonin (**6**) was hydrogenated under similar conditions, one

(1) For the previous paper in this series, see THIS JOURNAL, **80**, 5704 (1958).

(2) Du Pont Teaching Fellow, 1956–1957.

(3) W. G. Dauben and P. D. Hance, THIS JOURNAL, **77**, 606 (1955).

(4) W. G. Dauben and P. D. Hance, *ibid.*, **77**, 2451 (1955).

(5) W. G. Dauben, P. D. Hance and W. K. Hayes, *ibid.*, **77**, 4609 (1955).

(6) N. W. Chopra, W. Cocker, B. E. Cross, J. T. Edward, D. H. Hayes and H. P. Hutchinson, *J. Chem. Soc.*, 588 (1955).

(7) N. W. Chopra, W. Cocker, J. T. Edward, T. B. H. McMurry and E. R. Stuart, *ibid.*, 1828 (1956).

(8) In this present work, the previously defined santanic acid nomenclature[3] is used but has been modified so that the numbering of the positions resembles that of a steroidal system rather than a decalin system.

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