aqueous solution of potassium sodium tartrate. The slurry was stirred for 2.25 hr., and the precipitate was removed by filtration and washed several times with ether. After the combined ether solutions were dried over magnesium sulfate, the ether and by-product alcohols were removed by distillation through a 12-in. Vigreux column. The residue was fractionally distilled through the same column to yield 96.3 g. (75%) of 2-hydroxy-3-cyclohexene-1-methanol (VIII), b.p. 117° (2.6 mm.), n^{25}_{D} 1.5081.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.32; H, 9.34.

2-Acetoxy-3-cyclohexene-1-methyl acetate (IX). To a 2-l., three-necked flask, fitted with a dropping funnel and a condenser and containing 605 ml. (6.4 moles) of hot acetic anhydride, was added a solution of 204 g. (1.59 moles) of 2-hydroxy-3-cyclohexene-1-methanol (VIII) in 92 ml. (1.6 moles) of glacial acetic acid over a period of 1 hr. After the solution had been heated under reflux for 16 hr., the acetic acid and acetic anhydride were removed by distillation through a 12-in., helix-packed column under reduced pressure. The residue was fractionally distilled through the same column to yield 321 g. (95%) of 2-acetoxy-3-cyclohexene-1-methyl acetate (IX), b.p. 124° (3.4–3.5 mm.), n^{25}_{D} 1.4612.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.59. Found: C, 62.46; H, 7.48.

Pyrolysis of 2-acetoxy-3-cyclohexene-1-methyl acetate (IX). Preliminary pyrolysis of 2-acetoxy-3-cyclohexene-1-methyl acetate (IX) at 450° indicated that 1.5 molar equivalents of acetic acid had been eliminated and the pyrolysate contained a mixture of toluene, 3-methylenecyclohexene (VI) and bibenzyl. For this reason, 149 g. (0.702 mole) of IX was dropped through the pyrolysis tube at 378–383° over a period of 5.5 hr. and a solution of the pyrolysate in 350 ml. of ether was washed with a solution of 35 g. of sodium carbonate monohydrate in 175 ml. of water. (In a parallel run, when the pyrolysate solution was extracted exhaustively with water, titration of aliquots of the aqueous washings showed that 55% of one molar equivalent of acetic acid had been liberated.) After the ether extracts were dried over magnesium sulfate, the solvent was removed at atmospheric pressure through a 12-in. Vigreux column. The residue was fractionally distilled through the same column to yield 46.0 g. (43%) of a mixture of diene acetates, b.p. 72–74° (5.6–4.2 mm.), n^{25}_{D} 1.4809, and 68.7 g. (46% recovery) of unsaturated diacetates, b.p. 118–124° (4.0 mm.), n^{25}_{D} 1.4641. The yield of diene acetates, based on unrecovered starting material, was therefore 80%.

Refractionation of the mixture of diene acetates through an 18-in., Podbielniak-type column afforded only a partial separation. As the index of refraction of the fractions passed through a minimum, at least three components were present. Elemental analysis showed the presence of a nonisomeric impurity. The ultraviolet spectra of all fractions showed absorption in the vicinity of 260 mμ; a second maximum near 230 mμ appeared only in the lower boiling fractions. A fraction, b.p. 64.5° (3.6–3.7 mm.), n^{25}_{D} 1.4790; ϵ_{max} 4260 at 257.5 mμ; ϵ_{max} 4720 at 232.5 mμ, was subjected to infrared analysis. The spectrum was qualitatively similar to that of 4-methylene-2-cyclohexenyl acetate (V), but the intensity of the band at 891 cm.$^{-1}$ was substantially diminished.

Further pyrolysis of this mixture of diene acetates at 460–465° yielded toluene, 3-methylenecyclohexene (VI), and bibenzyl.

In a small Erlenmeyer flask fitted with a reflux condenser were placed 1.23 g. (0.0125 mole) of maleic anhydride, 2.04 g. (0.0134 mole) of the mixture of diene acetates described above, 6 ml. of dry benzene, and a small amount of hydroquinone. After the solution was heated on a steam bath for 13.5 hr., the solvent was removed by evaporation in a current of air, and the residue was dissolved in a mixture of toluene and petroleum ether. The solution was chilled in a Dry Ice–Methyl Cellosolve bath, and the very viscous material which separated was discarded. The supernatant liquid was decanted and was freed of solvents by evaporation. The resulting residue was dissolved in ether and chilled in the Dry Ice–Methyl Cellosolve bath to yield, after recrystallization from a mixture of ether and acetone, 0.22 g. (7%) of a crystalline adduct, m.p. 122.5–124°.

Anal. Calcd. for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.58; H, 5.71.

The infrared spectrum (in carbon disulfide) included strong bands at 1780, 1739, 1218, 946, and 909 cm.$^{-1}$ and weak bands at 1080 and 786 cm.$^{-1}$.

Vulgarin, a Sesquiterpene Lactone from *Artemisia vulgaris* L.

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Vulgarin, a sesquiterpenoid lactone from *Artemisia vulgaris* L., has been shown to have the structure III.

In the course of the examination of various genera of the Compositae for alkaloids, a crystalline compound was isolated from an Australian specimen of *Artemisia vulgaris* L.[1] This substance, now called vulgarin, was nonnitrogenous and gave an intense purple coloration in the hydroxamic acid test. This behavior, coupled with its composition, expressed in the formula $C_{15}H_{20}O_4$, suggested that it was a sesquiterpenoid lactone and a new member of the group of these substances in which the genus *Artemisia* abounds. The recent description[2] of a compound called tauremisin-A, from *Artemisia taurica*, leads us to believe that vulgarin and tauremisin-A are the same compound (m.p., rotation, spectral properties), but Rybalko *et al.* have not recorded sufficient additional information to confirm this identity.

Vulgarin, obtained from the dry plant in 0.15% yield, has m.p. 174–175°, $[\alpha]^{27}_{5461}$ + 48.7°, and strong infrared absorption at 3520 (hydroxyl), 1775 (γ-lactone), and 1665 cm.$^{-1}$ The ultraviolet

[1] The compound was first obtained as a crystalline material by Dr. C. C. J. Culvenor, C.S.I.R.O., Melbourne, to whom we are grateful for calling it to our attention and for providing additional plant material for our study.

[2] K. S. Rybalko, A. I. Ban'kovskii, and M. E. Perel'son, *Med. Prom. U.S.S.R.*, **14**, No. 10, 21 (1960).

absorption maximum of 215 mμ (ϵ 10,400) is rather lower than would have been anticipated for a cyclohexenone, as vulgarin has been found to be, and the single peak in the infrared at 1665 cm.$^{-1}$ is unaccompanied by definite carbon-carbon double bond absorption. Vulgarin forms an oxime and a 2,4-dinitrophenylhydrazone which had λ_{max} 369 mμ (ϵ 28900). This value, too, is rather lower than is usual for the absorption maxima of dinitrophenylhydrazones of α,β-unsaturated ketones, although it is definitely higher than those typical of saturated ketones.[3] The carbon-methyl value of 2.35 was in accord with the view that vulgarin was terpenoid in nature. The compound gave a positive Baeyer test (potassium permanganate in ethanol) but did not readily decolorize bromine in carbon tetrachloride.

Hydrogenation of vulgarin in ethyl acetate with 10% palladium on charcoal resulted in the smooth uptake of one mole of hydrogen and the formation of dihydrovulgarin. The dihydro compound showed no significant ultraviolet absorption and had infrared bands at 3520 (hydroxyl), 1775 (γ-lactone), and 1705 cm.$^{-1}$ (cyclohexanone). It gave a 2,4-dinitrophenylhydrazone with λ_{max} 361 (ϵ 16,000), and showed 1.95 C-methyl groups.

When the hydrogenation of vulgarin was carried out in acetic acid, two moles of hydrogen were absorbed, the second much more slowly than the first, and the reduction was not complete (as shown by analytical results and infrared absorption) at atmospheric pressure. Hydrogenation in acetic acid at 50 p.s.i. gave pure tetrahydrovulgarin, which no longer contained a carbonyl group as shown by the absence of absorption in the 1700-cm.$^{-1}$ region (bands at 3520 and 1775 cm.$^{-1}$).

It was clear from this result that vulgarin contained one carbon-carbon double bond, a carbonyl group, and a γ-lactone grouping, and the summary of the foregoing evidence was that the compound is a naphthalenogenic sesquiterpene of the santonin group. Confirmation of the fact that in tetrahydrovulgarin the carbonyl group had been reduced was obtained by reoxidation of tetrahydrovulgarin to dihydrovulgarin with chromic acid.

The hydroxyl group of vulgarin was clearly in a tertiary position, for attempted acetylation with acetic anhydride–pyridine and acetic anhydride–sodium acetate failed, and vulgarin was recovered unchanged after attempted oxidation with chromium trioxide–pyridine.[4] That the hydroxyl group was in the γ-position to the α,β-unsaturated ketone was strongly indicated by the abnormally low wave length of the ultraviolet absorption[5]; in addition, it was likely from this same property that the double bond was of the type —CH=CH—. The conclusion was shown to be correct by examination of the NMR spectrum[6] (see Fig. 1): vulgarin showed a pair of well defined doublets τ = 3.33, 3.50 and 4.09, 4.25. The NMR spectrum in the vinyl hydrogen region was almost identical with that of the α-epoxide of santonin, which has been shown[7] to have the structure containing the grouping —CH=CH=CO—.

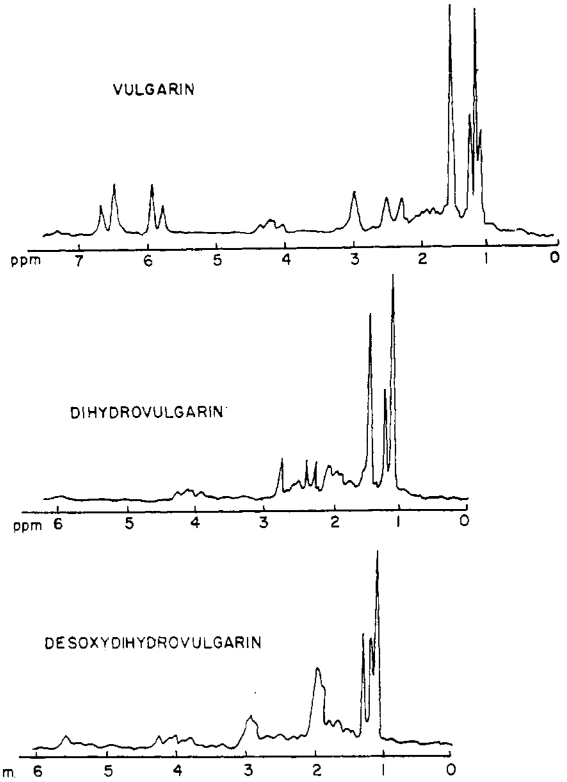

Fig. 1. NMR spectra of vulgarin, dihydrovulgarin, and desoxydihydrovulgarin (60 mc., solvent deuterochloroform)

In addition the NMR spectrum of vulgarin showed clearly three C-methyl groups with singlets at 8.46 and 8.81 with a doublet at 8.78 (J = 7.8 cycles/sec.). The NMR of dihydrovulgarin also showed three C-methyls with singlets at 8.49 and 8.83 with a doublet at 8.78 (J = 6 cycles/sec.). Both vulgarin and dihydrovulgarin showed a pair of doublets superimposed on one another at 5.81 and 5.99 (J = 8.40 and 7.80 cycles/sec.) indicative of a proton flanked on both sides by a tertiary hydrogen.

Dehydration of vulgarin with glacial acetic acid containing a trace of sulfuric acid yielded a crystalline mixture of dehydrovulgarins. This material had infrared bands at 1775 (γ-lactone),

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(3) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

(4) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 428 (1953).

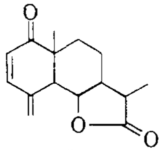
(5) T. G. Halsall, W. J. Rodewald, and (in part) D. Willis, *J. Chem. Soc.*, 1959, 2798.

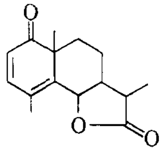
(6) NMR spectra were determined in deuterochloroform at 60 mc. with tetramethylsilane as internal references. The tau values were determined by the side-band technique.

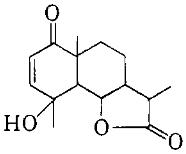
(7) J. B. Hendrickson and T. L. Bogard, private communication.

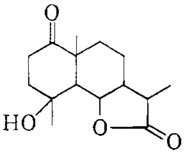
1665 (unsaturated ketone), 1625, and 1588 cm.$^{-1}$ (conjugated carbon-carbon double bonds). The ultraviolet spectrum showed two maxima at 270 (ϵ 6050) and 320 (ϵ 2340) mμ, and a Kuhn-Roth determination showed a C-methyl value of 1.58. The NMR spectrum showed four vinyl hydrogens; two of these corresponded to those observed in vulgarin, and the other two were in a position that marked them as present in an exocyclic methylene group. The methylenic hydrogens corresponded closely in their position in the NMR spectrum to those in another sesquiterpenoid lactone, bigelovin,[8] in which the exocyclic methylene group is known to be present.

The anhydrovulgarins thus appear to have the following structures (I, II) and vulgarin and dihydrovulgarin are III and IV.


I


II

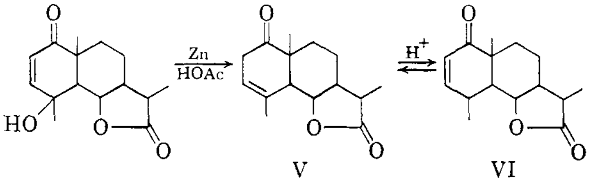

III


IV

In accord with structure IV, dihydrovulgarin gave iodoform when treated with sodium hypoiodite. This reaction, which is also observed in the cases of dihydrocarvone hydrate, carvone hydrate, and dihydrophotosantonic lactone.[9]

Reduction of vulgarin with zinc and acetic acid[5] removed the hydroxyl group and gave desoxyvulgarin (V), a β,γ-unsaturated ketone with infrared bonds at 1775 and 1705 cm.$^{-1}$, and no ultraviolet maximum (ϵ 2130 at 210 mμ). Desoxyvulgarin had no well defined infrared band corresponding to the carbon-carbon double bond, but it gave a positive Baeyer test, absorbed bromine in carbon tetrachloride, and took up one mole of hydrogen with the formation of dihydrodesoxyvulgarin (VII). The NMR spectrum of desoxyvulgarin again showed three C-methyls with singlets at 8.05 and 8.88 with a doublet at 8.79 ($J = 7.2$ cycles/sec.). A vinyl hydrogen peak at 4.45 was also present which appeared to be an unresolved triplet. (see Fig. 1).

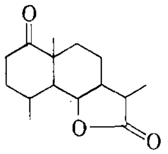
An attempt to isomerize desoxyvulgarin to the α,β-unsaturated isomer (VI) with acetic acid–acetic anhydride containing a trace of perchloric acid[10] resulted in the formation of a new crystalline product of broad melting point with an ultraviolet absorption of 225 mμ (ϵ 4240) and infrared bands at 1775, 1705, and 1665 cm.$^{-1}$. It is probable that an equilibration (V, VI) occurred, accounting for the low extinction at the ultraviolet absorption maximum and the appearance of two carbonyl bands in the infrared.

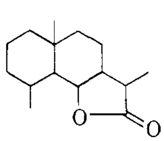


V VI

A similar mixture of α,β- and β,γ-unsaturated ketones was formed when dehydrovulgarin (IV) was dehydrated. The product melted over a narrow range (112–115°) but had an ultraviolet absorption maximum of 225 (ϵ 2250) and infrared bands at 1775, 1705, and 1675 cm.$^{-1}$ (the latter two of reduced intensity).

The position assigned to the lactone ring has been chosen because of the nearly identical infrared spectra of desoxydihydrovulgarin (VII) and tetrahydrosantonin,[11] and the close similarity of the infrared spectra of desoxodesoxydihydrovulgarin (VIII) (a santanolide) and santanolide-a.[16] The two are not the same, however; they have quite different specific rotations and the mixed m.p. shows a 30° depression. The superimposed doublets in the 5.80 region in the NMR spectrum of vulgarin, dihydrovulgarin, and desoxyvulgarin substantiate the above conclusions and clearly rule out the possibility of the lactone being as in alantolactone (*i.e.*, closed to C-7 rather than C-5).


VII


VIII

The stereochemistry of vulgarin remains to be determined, but one stereochemical feature appears to be established. The dehydration of vulgarin to a dehydrovulgarin containing a large proportion of the exomethylenic isomer suggests that the hydroxyl group at position 4 is *cis* to the hydrogen atom at the ring junction (position 5). There is no evidence concerning the stereochemistry of the ring fusion and no assumption of the point is convincing, since the carbonyl group cannot affect this by enolization. If, however, the tentative assumption is made that the A/B ring fusion is

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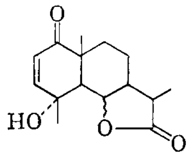
(8) T. A. Geissman and B. A. Parker, unpublished results.

(9) D. H. R. Barton, S. K. Pradhan, S. Sternbell, and J. F. Templeton, *J. Chem. Soc.*, 255 (1961).

(10) D. H. R. Barton, O. C. Bockman, and P. de Mayo, *J. Chem. Soc.*, 2263 (1960).

(11) The comparison was made with a specimen of tetrahydrosantonin prepared by Mr. T. L. Bogard in the course of another investigation.[7]

trans, as in eudesmol and alantolactone,[12] vulgarin is provisionally represented by IX:



IX

Further study of the stereochemistry of the lactone is in prospect.[13]

EXPERIMENTAL[14]

Vulgarin (III). *Isolation.* Dry, milled whole plant of *Artemisia vulgaris* L. (1000 g.) was covered with chloroform and the slurry allowed to stand for two days. The mixture was filtered and the mash washed with several portions of fresh chloroform. The solvent was removed under reduced pressure, and the residual tar was dissolved in 70 ml. of ethanol to form a thin syrupy solution, to which 200 ml. of hot water was added. The mixture was shaken vigorously and allowed to cool somewhat. Tarry material coagulated and was removed by decantation. The tar was treated again with ethanol-water in the same way.

The aqueous ethanolic extract was treated several times with Celite-Norite and the final filtrate extracted repeatedly with chloroform. The yellow chloroform extract was dried with magnesium sulfate and evaporated under reduced pressure. The oily residue crystallized when rubbed with ether, affording 1.5 g. of crystalline vulgarin. Recrystallized from alcohol, the compound formed colorless needles, m.p. 174–175°. The lactone gave an intense purple color in the hydroxamic acid test. It had $[\alpha]^{27}_{5461}$ + 48.7 (*c* 3.86, $CHCl_3$), and had λ_{max} 215 mμ (ε 10400) and infrared bands at 3250, 1775, and 1665 cm.$^{-1}$. It gave a C-methyl number of 2.33.[15]

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.55; 68.21; H, 7.94; 7.65.

Vulgarin formed a *2,4-dinitrophenylhydrazone*, yellow-orange needles, m.p. 275° dec., λ_{max} 369 (ε 28900).

Anal. Calcd. for $C_{21}H_{24}O_7N_4$: C, 56.76; H, 5.40. Found: C, 56.68; H, 5.44.

The *oxime* of vulgarin had m.p. 260–262°.

Anal. Calcd. for $C_{15}H_{21}O_4N$: C, 64.52; H, 7.53. Found: C, 64.31; H, 7.36.

Vulgarin readily decolorized potassium permanganate in ethanol (Baeyer test) but did not absorb bromine in carbon tetrachloride. Attempts to acetylate the compound (acetic anhydride with pyridine or sodium acetate) resulted only in the recovery of unchanged vulgarin.

Dihydrovulgarin (IV). A solution of 0.66 g. of vulgarin in ethyl acetate was hydrogenated in the presence of 100 mg. of 5% palladium-charcoal. After 35 minutes the uptake of hydrogen was 60 ml. (equivalent to 1 mole). The catalyst was removed and the filtrate evaporated to a crystalline residue. Recrystallized from ethanol, the compound had m.p. 172–173° (mixed with vulgarin, the m.p. was depressed only slightly). The dihydro compound showed 1.95 C-methyl groups and had $[\alpha]^{27}_{5461}$ −48.9 (*c* 4.25, $CHCl_3$). The infrared spectrum showed bands at 3520, 1775, and 1705 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{22}O_4$: C, 67.67; H, 8.33. Found: C, 67.92; H, 8.40.

The *2,4-dinitrophenylhydrazone* of dihydrovulgarin had m.p. 280° dec. and λ_{max} 361 mμ (ε 16,000).

Anal. Calcd. for $C_{21}H_{26}O_7N_4$: C, 56.40; H, 5.83. Found: C, 56.44; H, 5.72.

Tetrahydrovulgarin. A solution of 0.26 g. of vulgarin in acetic acid was hydrogenated at 50 lbs. pressure with platinum oxide as the catalyst. Removal of the catalyst and the solvent afforded 0.145 g. of crude tetrahydrovulgarin, m.p. 186–187°. Recrystallization from ethyl acetate separated the tetrahydro compound from traces of dihydrovulgarin, recognized by the small band at 1705 cm.$^{-1}$ in the infrared spectrum of the crude material. Tetrahydrovulgarin melted at 197–199°, and had infrared bands at 3520 and 1775 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01. Found: C, 66.85; H, 8.81.

Oxidation of tetrahydrovulgarin. To a solution of 100 mg. tetrahydrovulgarin in 40 ml. of acetic acid was added 2.81 ml. of a 2% solution of chromium trioxide in acetic acid. After 16 hr. a few drops of methanol were added to destroy excess chromium trioxide and the solvent was removed under reduced pressure. The residue crystallized when stirred with a few drops of water. Recrystallization afforded 62 mg. of dihydrovulgarin, m.p. 170–171°, not depressed upon admixture with authentic material. The infrared spectra of the two specimens were identical.

Anal. Calcd. for (oxidation product) $C_{15}H_{22}O_4$: C, 67.67; H, 8.33. Found: C, 67.53; H, 8.22.

Dihydrodesoxyvulgarin (VII). The dihydrovulgarin from the hydrogenation of 1.34 g. of vulgarin was dissolved in acetic acid containing a trace of concentrated sulfuric acid. The solution was heated on the steam bath for 20 min. and poured into ice water. After neutralization of the acids with 5% sodium hydroxide, the solution was extracted with chloroform. The dried chloroform solution was evaporated to an oil which crystallized on trituration with ether. The crude product (m.p. 109–111°), without further purification, was dissolved in ethyl acetate–acetic acid and hydrogenated over platinum. The reaction was interrupted after 75 ml. (1 mole) of hydrogen had been absorbed. Upon isolation of the product in the usual way there was obtained 0.73 g. of dihydrodesoxyvulgarin, white needles from ethanol, m.p. 199–200°. The compound had $[\alpha]^{27}_{5461}$ +74.3 (*c* 3.50, $CHCl_3$) and showed infrared bands at 1775 and 1705 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.96; H, 8.66. Found: C, 71.85; H, 8.81.

Santanolide-x (VIII) *from vulgarin.* Dihydrodesoxyvulgarin, 0.5 g., was reduced by the Clemmensen procedure as described by Kovacs *et al.*[16] After refluxing for 12 hr., the solution was extracted with ether and the ether layer dried and evaporated. The residue was recrystallized from 90% ethanol as colorless flakes, m.p. 153–154°. The product had

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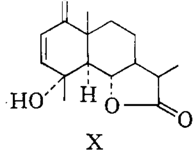
(12) K. Tanabe, *Pharm. Bull.* (Japan), 5, 263 (1957).

(13) A private communicaton from Dr. V. Herout, received since this manuscript was submitted, has substantiated the identity of tauremisin-A and vulgarin and that their structural conclusions are identical with ours. Further, they have found that "santanolide-c", previously reported by Sorm's school[16] as having m.p. 137–138°, has m.p. 155° (see Experimental) and is identical with the santanolide from vulgarin/tauremisin. This of course completes the definition of the stereochemistry, and the compound can be represented as X:



X

(14) Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared spectra were taken in chloroform solution using a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were taken in 95% ethanol using a Cary Model 14 spectrophotometer.

(15) W. T. Smith and R. L. Shriner, "The Examination of New Organic Compounds," John Wiley and Sons, New York, 1956.

(16) O. Kovacs, V. Herout, M. Horak, and F. Sorm, *Coll. Czech. Chem. Comm.*, 21, 225 (1956).

$[\alpha]^{27}_{5461}$ +69.25 (*c* 3.97, $CHCl_3$) and showed a prominent infrared band at 1775 cm.$^{-1}$ but no other bands in the carbonyl or double-bond region. The infrared spectrum had a remarkably close resemblance to that of santanolide-a, prepared from santonin.[11] The melting point of a mixture of the two santanolides was depressed about 30°.[17]

Anal. Calcd. for $C_{15}H_{24}O_2$: C, 76.27; H, 10.17. Found: C, 76.18; H, 10.13.

Desoxyvulgarin (V). To a boiling solution of 0.33 g. of vulgarin in 15 ml. of acetic acid was added 0.5 g. of powdered zinc over the course of 20 min. The cooled solution was filtered and the zinc washed with chloroform. Evaporation of the solution left a semicrystalline residue which was taken up in chloroform and the solution washed with aqueous sodium bicarbonate and water, dried, and evaporated. The product (0.23 g.) formed white crystals, m.p. 138–139°, and had $[\alpha]^{27}_{5461}$ + 75.2° (*c* 3.13, $CHCl_3$) and infrared bands at 1775 and 1705 cm.$^{-1}$. The compound gave a positive Baeyer test and readily decolorized a solution of bromine in carbon tetrachloride.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.58; H, 8.06. Found: C, 72.70; H, 8.28.

Equilibration of desoxyvulgarin (V $\rightleftharpoons$ VI). A solution of desoxyvulgarin from 0.5 g. of vulgarin in a mixture of 20 ml. of acetic acid, 2.5 ml. of acetic anhydride, and 2 drops of 70% perchloric acid was heated on a steam bath for 15 minutes. The product, isolated as described above for the isolation of desoxyvulgarin, formed colorless crystals from ethanol, m.p. 105–110°. The compound had infrared bands at 1775, 1705, and 1665; its ultraviolet absorption maximum was at 225 mμ (ϵ 4280).

Dihydrodesoxyvulgarin (VII) *from desoxyvulgarin.* Hydrogenation of 73 mg. of desoxyvulgarin in ethyl acetate–acetic acid (1:1) over platinum resulted in the ready uptake of 1 mole of hydrogen. The product, isolated in the usual way, was dihydrodesoxyvulgarin, m.p. 199–200°, identical in mixed m.p. and infrared spectrum with the compound prepared by the reduction of the dehydration product of dihydrovulgarin.

Iodoform from dihydrovulgarin. Treatment of dihydrovulgarin with sodium hypoiodite in the usual way[18] gave a poor yield of iodoform, isolated in the crystalline state and having the same m.p. as authentic iodoform, undepressed on mixing.

Anhydrovulgarin (I, II). A solution of 0.40 g. of vulgarin in 10 ml. of acetic acid containing 3 drops of concentrated sulfuric acid was warmed on a steam bath for 10 min. The solution was cooled, poured onto ice, neutralized with sodium hydroxide, and extracted with chloroform. After drying and concentrating the chloroform solution, it was passed through alumina (activity 4), eluting with ether-benzene. The residue from the eluant was crystallized from aqueous ethanol to give colorless needles, m.p. 115–125°. The infrared spectrum showed bands at 1775, 1665, 1625, and 1588. The C-methyl number was 1.58. The ultraviolet spectrum showed two maxima: 270 mμ (ϵ 6050) and 320 (ϵ 2340).

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.28; H, 7.39.

Dihydrodesoxyvulgarin (VII) *from anhydrovulgarin.* A sample of 1.03 g. of vulgarin was dehydrated as just described, and the crude product hydrogenated over platinum in ethyl acetate containing some acetic acid. The product from this series of operations showed some hydroxyl absorption in the infrared, and the 1705-cm.$^{-1}$ band was of diminished intensity, indicating that some reduction of the carbonyl group had taken place. The crude product was oxidized with chromic acid (9.5 ml. of a 2% solution in acetic acid) in acetic acid (36 ml.) overnight. The product, isolated in the usual way, was dihydrodesoxyvulgarin (m.p. and mixed m.p., identical infrared spectra).

Desoxyvulgarin (VII) *from dihydrovulgarin.* A solution of 0.50 g. of dihydrovulgarin (IV) in 10 ml. of acetic acid containing 10 drops of concentrated sulfuric acid was warmed for 10 min. on the steam bath. The product, isolated in the usual way, formed 0.29 g. of pale yellow crystals, m.p. 95–104°. After three recrystallizations from ethanol the m.p. rose to 112–115°. The compound showed infrared bands at 1775, 1705, and 1675 cm.$^{-1}$ and had λ_{max} 225 mμ (ϵ 2280).

Anal. Calc. for $C_{15}H_{20}O_3$: C, 72.58; H, 8.06. Found: C, 72.70; H, 7.95.

Attempted oxidation of vulgarin. To a solution of 0.23 g. of chromium trioxide in 2.3 ml. of dry pyridine was added 0.186 g. of vulgarin. The mixture was stirred at room temperature for 16 hr., poured into water, and extracted with chloroform. The dried chloroform solution was evaporated to give unchanged vulgarin in good yield.

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(17) The melting point reported[16] for santanolide-c was 139°. This has now been corrected to 155° (private communication from Dr. V. Herout—see above).

(18) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed. (rev.), D. C. Heath and Co., Boston, 1957, p. 86.