[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

Constituents of Helenium Species. VI. Correlation of Helenalin and Alloisotenulin[1]

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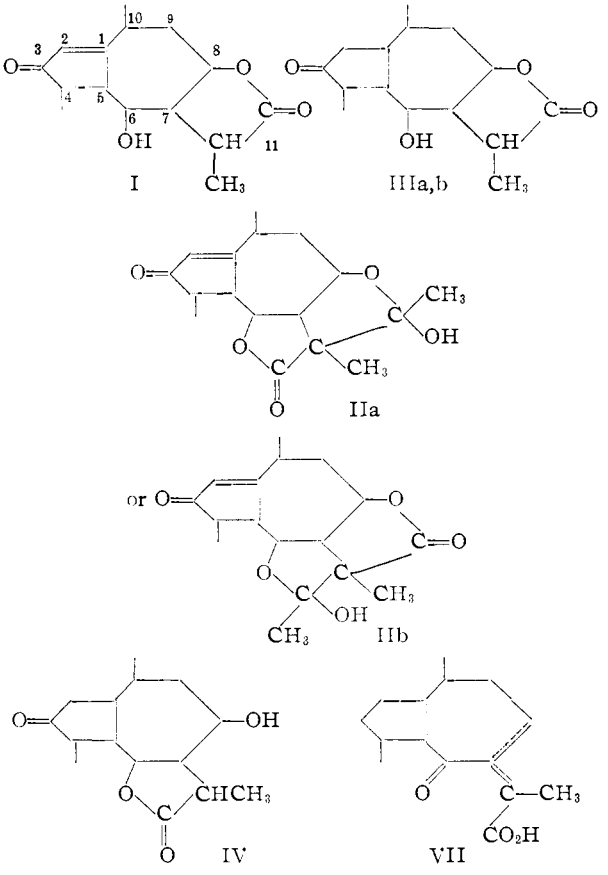
Helenalin has been isolated from *Actinospermum angustifolium* (*Balduina angustifolia*). The conversion of tetrahydrohelenalin to an acid previously obtained from desacetyldihydroalloisotenulin establishes the common gross structure and identical stereochemistry at C_1, C_4, C_5 and C_{10} of these two substances. The configuration of the other asymmetric centers is discussed.

The main structural features of helenalin (I)[2] and tenulin (II),[1,3,4] the bitter principles of various *Helenium* species, have been elucidated recently, although certain details remain to be clarified.[5] It is particularly desirable to determine the structural and stereochemical features which differentiate tetrahydrohelenalin (IIIa)[1,2,6] from two isomeric compounds of the tenulin series, desacetyldihydroisotenulin (III or IV)[3,4] and desacetyldihydroalloisotenulin (IIIb).[4] Optical rotatory dispersion studies[1] indicated that helenalin and tenulin, as well as their reduction products, belong to the same stereochemical series insofar as the ring junction (C-1 and C-5) is concerned; differences must therefore be sought elsewhere. The information presented in this paper is designed to bear on this problem.



In the course of our work on the phytochemistry of certain plants of the Tallahassee area we had occasion to investigate *Actinospermum angustifolium* (Pursh) T. and G., a bitter herb found in the pine lands and sandy soils of southern Georgia and northern Florida.[7] To our surprise, extraction with chloroform yielded as the main constituent helenalin. This suggests that the genus *Balduina*, although technically placed in a tribe of *Compositae* different from *Heleniae* (the tribe containing the genus *Helenium*), is more closely related to *Helenium* than has generally been supposed.[8]

Having come into possession of a small supply of helenalin, we thought that it might be possible to convert tetrahydrohelenalin to a derivative of tenulin by reducing the number of functional groups and asymmetric centers. This would establish the relationship deduced by optical methods. The most likely candidate compound was the acid VIIb which had been obtained previously[4] by treatment of dehydrodesoxodesacetyldihydroalloisotenulin (VIb) with sodium carbonate. It already has been mentioned that rotatory dispersion measurements indicated the equivalence of the asymmetric centers at C-1 and C-5, and by implication at C-4; furthermore, during the conversion of III to VIIb, the asymmetric centers of C-6, C-7 and C-8 disappear. If tetrahydrohelenalin and desacetyldihydroalloisotenulin possess the same gross structure III, any differences between VIIb and the hypothetical analog of the helenalin series would then be restricted to asymmetry at C-10, a possibility which seemed slight, and, depending upon the position of the double bond, *cis–trans* isomerism around C-7–C-11 or asymmetry at C-11.

As shown in the accompanying flowsheet, the thioketal of tetrahydrohelenalin on desulfurization yielded an oily hydroxylactone, desoxotetrahydrohelenalin (Va), which was oxidized to a crystalline dehydrodesoxotetrahydrohelenalin (VIa). Treatment of VIa with sodium carbonate resulted in opening of the lactone ring and gave an unsaturated ketoacid VIIa which resembled VIIb, but was not identical with it.

(1) Previous paper, C. Djerassi, J. Osiecki and W. Herz, *J. Org. Chem.*, **22**, 1361 (1957). The papers by R. Adams and W. Herz, THIS JOURNAL, **71**, 2546, 2551, 2554 (1949), are considered as the first three papers of this series.

(2) G. Büchi and D. Rosenthal, *ibid.*, **78**, 3860 (1956).

(3) D. H. R. Barton and P. DeMayo, *J. Chem. Soc.*, 142 (1956).

(4) B. H. Braun, W. Herz and K. Rabindran, THIS JOURNAL, **78**, 4423 (1956).

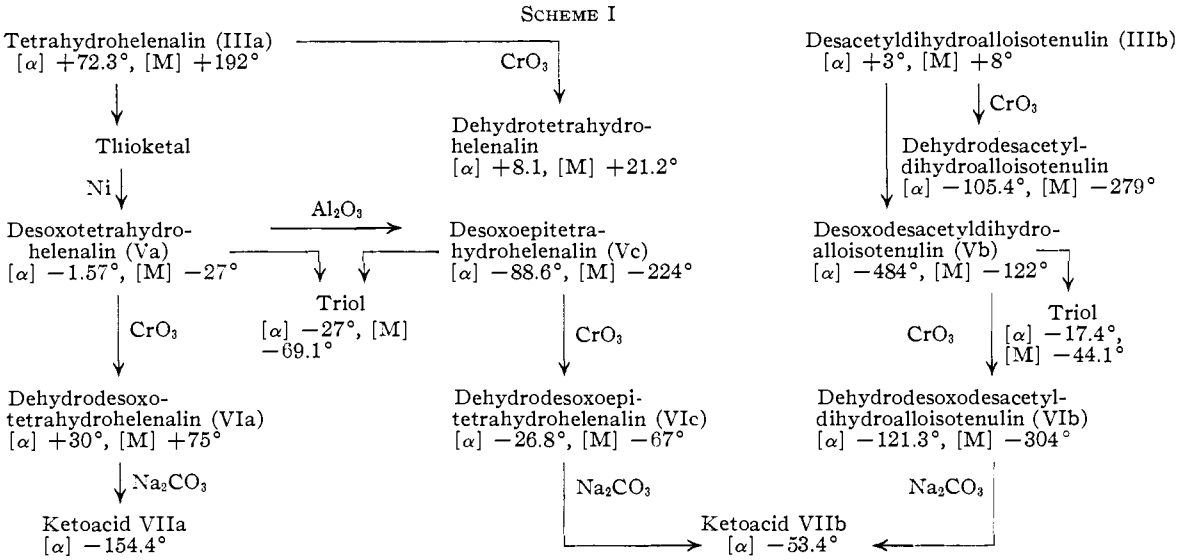
(5) For comments on this, see D. H. R. Barton and P. DeMayo, *Quart. Revs.*, **11**, 189 (1957). In the following the orientation of the lactone ring of helenalin will be assumed as having been established and will serve as reference.

(6) E. P. Clark, THIS JOURNAL, **61**, 1836 (1939); **62**, 597, 2154 (1940).

(7) According to Dr. Howard F. S. Rock of the Department of Botany, University of Tennessee, *A. angustifolium* is identical with *Balduina angustifolia* and should be listed under the latter name.

(8) We are grateful to Dr. Rock for informing us that he has reached the same conclusion earlier on the basis of cytological studies.

SCHEME I



When attempts were made to crystallize Va by chromatography over alumina, it was isomerized to desoxoepitetrahydrohelenalin (Vc), a change which also could be effected by treatment with dilute base. Since alumina would not be expected to cause opening of the lactone ring, the conversion of Va to Vc most likely involves epimerization at C-11.[9] Oxidation of Vc with chromium oxide furnished dehydrodesoxoepitetrahydrohelenalin (VIc) which was isomeric with VIa and VIb. Upon treatment of VIc with sodium carbonate there was formed an unsaturated ketoacid *which was identical in all respects with authentic VIIb*.

The successful conversion of IIIa to VIIb establishes not only that tetrahydrohelenalin (IIIa) and desacetyldihydroalloisotenulin (IIIb) have the same gross structure, but that the stereochemistry at C-1, C-4, C-5 and C-10 is identical.[10] A slight reservation remains about the stereochemistry at C-5 which could conceivably have been epimerized in the course of Na_2CO_3 treatment of VIb or VIc. Earlier evidence[1] suggests the contrary. Since VIa and VIc are different from VIb, it follows that IIIa and IIIb differ from each other at one or both of the asymmetric centers C-7 and C-8. But although IIIa apparently has the unstable configuration at C-11 (*viz.*, the conversion of Va to Vc),[11] whereas IIIb is stable, their relative configuration at C-11 is still uncertain. The uncertainty arises because of our lack of knowledge concerning the stereochemistry at C-7 and (or) C-8; the manner in which the lactone ring is fused onto the perhydroazulene system may profoundly influence the stability of the C-11 methyl group[12,13] (*vide infra*).

(9) See footnote 18 below.

(10) The stereochemistry of desacetyldihydroisotenulin (III or IV) at these four centers is thereby determined also, regardless of the orientation[5] of the lactone ring. We hope to present evidence bearing on the latter in a subsequent publication.

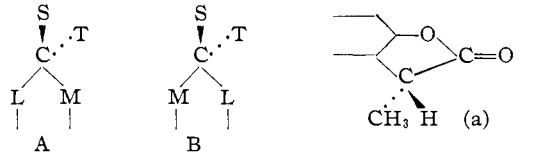
(11) Because IIIa is not epimerized by BF_3-etherate or Raney nickel, it is assumed that IIIa and Va have the same configuration at C-11. Now in contrast to Va, IIIa is not epimerized by alumina which indicates that the cyclopentanone carbonyl of IIIa exerts a positive influence on the stability of the C-11 methyl group.

(12) For an analogy in the ψ-santonin series, see N. M. Chopra, W. Cocker, J. T. Edward, T. B. H. McMurry and E. R. Stuart, *J. Chem. Soc.*, 1828 (1956).

Additional information concerning the stereochemical differences between IIIa and IIIb could conceivably be gleaned from optical data. It will be noticed from scheme I that the change in rotation which accompanies the oxidation of Va and Vc is of opposite sign to the change in rotation which results from the oxidation of Vb. Thus, Δ[M](VIa-Va) = 77.5°, Δ[M](VIc-Vc) = 157°, but Δ[M](VIb-Vb) = −182°. One might infer that the orientation of the C-6 hydroxyl group in the helenalin series is different from the orientation in desacetyldihydroalloisotenulin. This conclusion, however, would be valid only if the mode of attachment of the lactone ring which has been shown to be different (*vide supra*) were to have little effect on the conformation of the 7-membered ring.[15]

While the relative configuration of IIIa and IIIb at C-6 thus remains uncertain, it was thought that the lactone rule as modified by Klyne[16] concerning the rotatory contribution of the potential hydroxyl

(13) It is instructive to apply a rule recently formulated by Bose[14] to the two pairs of epimers Va and Vc, and VIa and VIc. If the absolute configuration of a pair of epimeric cyclic compounds (in which the ring is five or six-membered) be represented by A and B,



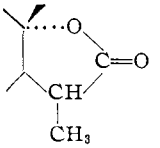
epimer A will be more dextrorotatory than B when L, M, S and T are in the decreasing order of their steric bulk in the immediate vicinity of the asymmetric carbon atom. Now at C-11, L = C-C-C, M = C = O, S = CH_3, T = H, and [M]Va > [M]Vc, and [M] VIa > [M] VIc. Hence the absolute configuration at C-11 of Va and VIa should be (a), that of Vc and VIc the opposite (but see below for evidence which suggests that VIa and VIc may differ at C-7 as well as C-11).

(14) A. Bose, Abstracts of Paris Congress, International Union of Chemistry, p. 141 (1957).

(15) That caution is necessary in interpreting these data is shown by the following. The change in rotation during the oxidation of tetrahydrohelenalin, [α] +72.3°, [M] +119.2°, to dehydrotetrahydrohelenalin, [α] +8.1°, [M] +21.2°, is of the same sign as the change which is observed when desacetylallodihydroisotenulin [M] +8°, is oxidized[4] to the dehydro analog, [M] −279°. The difference in magnitude suggests the presence of a second, superimposed effect which accounts for the reversal of sign in the helenalin series and which is eliminated on removal of the cyclopentanone function.

(16) W. Klyne, *Chemistry & Industry*, 1198 (1954).

group of the lactone ring might shed light on the stereochemistry at C-8. If the rule is applicable to guaianolides, as has been claimed recently,[17] desoxodesacetyldihydroalloisotenulin (Vb), [M] −122°, has the partial absolute configuration



because lithium aluminum hydride reduction furnishes a solid triol, [M] −44.1°. Now the change in rotation on converting Vc, [M] −224°, to a liquid triol, [M] −69°, is in the same direction.[18] Therefore, if the rule is valid, Va and Vc on the one hand[19] and Vb on the other have the same absolute configuration at C-8 and must differ at C-7. Since this center is destroyed on going to the acids VIIa and VIIb, the previous assumption that VIa and VIc are C-11 epimers (*vide supra*) offers a satisfactory rationale for the observation that VIa furnishes a ketoacid different from that produced by VIc and VIb.

The simple picture which emerges from these arguments is somewhat beclouded when one considers in addition the optical rotatory dispersion curves of VIa, VIb and VIc.[20] The curves of VIa and VIb are almost superimposable (single negative Cotton effect) except for a slight hypsochromic shift in VIb, whereas the curve of VIc is reflected around the horizontal axis (single positive Cotton effect), although its amplitude is considerably smaller. This indicates that VIb and VIc are of enantiomeric type which might be interpreted as confirming the conclusions reached earlier on the basis of Klyne's rule. But unless conformational effects due to the different orientation of the C-11 methyl group obtrude, one is also forced to conclude that VIa and VIb have the same configuration at C-7 and that VIa and VIc are enantiomeric at C-7.

One could account for this surprising result by assuming that chromic acid oxidation of Va is accompanied by epimerization at C-7, an assumption which could be supported by the following argument. The extremely facile change of Va to Vc is already indicative of a rather unstable spatial arrangement which can be relieved by epimerization at C-11. But in the ketolactone which is initially formed by oxidation of Va there exists a second, new path for relief of this strain under the influence of the acid medium. In view of the greater acidity of a hydrogen alpha to a ketone function, the second path, epimerization at C-7 *via* enolization, would be expected to take precedence over epimerization at C-11 which would be triggered by the lactone carbonyl. On the other hand, δ-tetrahydrosantonin is not converted to β-tetrohydrosantonin under similar conditions.[21] Although the stability relationships in the three series may be quite different, it is therefore uncertain whether the difference between the rotatory dispersion curves of VIa and VIc is due to conformational effects or to differences in absolute configuration at C-7.[22]

Acknowledgment.—We wish to thank Dr. Robert K. Godfrey of our Department of Botany for collecting the plant material. We are indebted to Eli Lilly and Company and the Research Corporation for financial support.

Experimental[23]

Isolation of Helenalin.—*Actinospermum angustifolium* (*Balduina angustifolia*) was collected in September, 1957, in the vicinity of Crestview, Florida, at the flowering stage. The dried whole plant, wt. 31 oz., was placed in two large Soxhlet extractors, each portion being extracted with 2.5 l. of chloroform for two days. After removal of the chloroform the residues were combined, dissolved in 300 ml. of 95% ethanol, mixed with a solution of 7 g. of lead acetate in 500 ml. of water and allowed to stand overnight. After filtration, the pale orange-brown solution was reduced to one-third of its volume on the water-pump and thoroughly extracted with chloroform. Removal of the chloroform furnished 13.7 g. of a viscous brown residue which was dissolved in benzene and chromatographed over alumina (40 g.). The eluate (benzene) gave a solid which on recrystallization from benzene afforded 5.75 g. of colorless crystalline material, m.p. 166–167°. There was no depression on admixture of an authentic sample of helenalin[24] and the infrared spectra were superimposable in every detail. From a total of 4 lb. 1 oz. of dried plant there was thus obtained 13.73 g. (0.53%) of helenalin which compares very favorably with the yield of helenalin from other sources.

Ethylene Thioketal of Tetrahydrohelenalin.—A mixture of 2.35 g. of IIIa and 2.3 ml. of ethanedithiol was treated with 4 ml. of boron trifluoride-etherate, swirled and let stand for 45 min. The homogeneous mixture was diluted with water, extracted with ether and the ether layer was washed with water, dilute aqueous sodium hydroxide, water again, dried and concentrated to 5 ml. when thick, heavy,

(17) V. Sykora and M. Romanuk, *Coll. Czech. Chem. Communs.*, **22**, 1908 (1957).

(18) Lithium aluminum hydride reduction of Va gave the same triol. Since Va and Vb are stereo- and not structural isomers, it is concluded that the reagent has effected epimerization at C-11.—D. S. Noyce and D. B. Denney, THIS JOURNAL, **72**, 5743 (1950), demonstrated retention of configuration during such reductions and no exceptions to this rule appear to have been recorded. However, there is no reason why a solution of the reagent which is basic should not be capable of epimerizing an extremely labile center like the one under discussion prior to reduction, particularly if it is situated next to a group whose reduction proceeds somewhat slowly. Several guaianolides are reduced with some difficulty under the usual conditions (Z. Čekan, V. Herout and F. Šorm, *Coll. Czech. Chem. Communs.*, **22**, 1717 (1957); W. Herz and W. A. Rohde, unpublished experiments), the isolable intermediate being a lactal which would also be subject to epimerization by a weak base if it were labile. The above result could be explained by assuming that Vc and VIc are structural isomers of Va and VIa and are formed by opening of the lactone ring and relactonization. This hypothesis would require opening and reclosure of the lactone ring by passage over alumina, which seems quite unlikely. Also, neither VIa nor VIc gives a positive Zimmermann test which indicates that the lactone ring is oriented similarly in both compounds.

(19) The mode of formation of Vc from Va would not be expected to affect the asymmetric center at C-8.

(20) We wish to thank Professor Carl Djerassi of Wayne State University for determining the rotatory dispersion data.

(21) J. C. Banerji, D. H. R. Barton and R. C. Cookson, *J. Chem. Soc.* 5041 (1957); see also D. N. Jones, J. R. Lewis, C. W. Shoppee and G. R. Summers, *ibid.*, 2876 (1955), for a similar situation.

(22) A change in conformation or epimerization at C-7 during the conversion of tetrahydrohelenalin to dehydrotetrahydrohelenalin[1] might conceivably account for the reversal of sign referred to in footnote 15. In any event, it now appears obvious that the difference in behavior of dehydrotetrahydrohelenalin[2,4] and dehydrodesacetyldihydroalloisotenulin[4] toward sodium carbonate solution (which leads, in the former case, by way of a remarkable cleavage, to a dibasic α,β-unsaturated ketoacid and in the latter case to formation of an acid presumably of type VII) arises not from a difference in gross structure but from a difference in stereochemistry.

(23) M.p.'s and b.p.'s are uncorrected. Infrared spectra were run on a Perkin–Elmer Model 21 double beam infrared spectrometer. Ultraviolet spectra were determined by Miss M. T. Esquivel on a Beckman Model DK1 recording spectrophotometer. Analyses by Drs. Weiler and Strauss, Oxford, England.

(24) Kindly furnished by Professor G. Büchi of the Massachusetts Institute of Technology.

colorless needles of the thioketal separated. Filtration and drying furnished 2.16 g. (79%), m.p. 119–120°. Recrystallization from aqueous methanol gave the analytical sample, m.p. 122°, containing one mole of water of crystallization.

Anal. Calcd. for $C_{17}H_{26}O_3S_2 \cdot H_2O$: C, 56.66; H, 7.78; S, 17.78. Found: C, 56.93; H, 7.65; S, 17.75.

Desoxotetrahydrohelenalin (Va).—A mixture of 1 g. of ethylene thioketal of IIIa and two teaspoons of Raney nickel in 150 ml. of absolute ethanol was refluxed under continuous mechanical stirring for 24 hours. The nickel was filtered, washed with hot ethanol, and from the combined alcoholic filtrate, solvent was removed to give Va as a thick viscous pale yellow oil, 0.82 g. (quantitative), $[\alpha]^{24}D$ −1.6° (95% ethanol, *c* 1.915); infrared bands at 3590, 3470 (free and bonded hydroxyl) and 1750 cm.$^{-1}$ (lactone). The substance was not analyzed because it could not be purified without partial epimerization to Vc.

Desoxoepitetrahydrohelenalin (Vc).—Chromatography of 0.22 g. of Va in benzene over 7 g. of basic alumina and elution with the same solvent furnished 0.21 g. of a crystalline solid, m.p. 161–163°. Three recrystallizations from aqueous methanol gave colorless long fine needles of Vc, m.p. 165°, $[\alpha]^{24}D$ −88.6° (95% ethanol, *c* 0.64); infrared bands at 3590 (free -OH), 3450 (broad, bonded -OH) and 1750 cm.$^{-1}$ (lactone).

Anal. Calcd. for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.19; H, 9.75.

Treatment of Va with sodium hydroxide also furnished Vc: 0.1 g. of Va was dissolved in 3 ml. of 10% aqueous sodium hydroxide by boiling for 3 min. The clear homogeneous solution was cooled and carefully acidified with hydrochloric acid. A semi-solid product which separated initially solidified on standing and was filtered, washed and dried and recrystallized from aqueous methanol to give colorless plates of Vc, 50 mg., m.p. 161–163°. A mixed m.p. with Vc obtained above was undepressed. A similar treatment of Vc with sodium hydroxide gave back starting material, albeit in poorer yield.

Dehydrodesoxotetrahydrohelenalin (VIa).—A solution of 1.2 g. of desoxotetrahydrohelenalin in 50 ml. of acetic acid was treated with 20 ml. of a 2% solution of chromic oxide in acetic acid (1.5 times theory) and allowed to stand overnight in the cold. Methanol was added to destroy excess chromic oxide and after removal of solvents under reduced pressure, the residue was treated with water when a crystalline solid separated. This was filtered, washed and dried to give 1.16 g. (97%) of VIa, m.p. 160–161°, unchanged on recrystallization from aqueous methanol, $[\alpha]^{24}D$ +30° (95% ethanol, *c* 0.61), infrared bands at 1775 lactone) and 1705 cm.$^{-1}$ (cycloheptanone). The substance gave a negative Zimmerman test.

Anal. Calcd. for $C_{51}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.31; H, 8.70.

Dehydrodesoxoepitetrahydrohelenalin (VIc).—A solution of 100 mg. of desoxoepitetrahydrohelenalin in 5 ml. of acetic acid was treated with 1.8 ml. of a 2% solution of chromic oxide in acetic acid and after working up the reaction mixture exactly as in the case of VIa there was obtained a white crystalline solid, 80 mg. (80%), m.p. 90–91°. Three recrystallizations from aqueous methanol gave shining colorless plates of VIc, m.p. 95–96°, $[\alpha]^{24}D$ −26.8° (95% ethanol, *c* 0.56), infrared bands at 1775 (lactone) and 1700 cm.$^{-1}$ (cycloheptanone). The substance gave a negative Zimmerman test.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.80; H, 8.88.

Attempts to obtain VIc by the epimerization of VIa on chromatography over basic alumina were unsuccessful; VIa was recovered together with some oily product that refused to crystallize from a number of solvents.

Sodium Carbonate-Treatment of Dehydrodesoxotetrahydrohelenalin.—A mixture of 0.5 g. of VIa and 0.8 g. of sodium carbonate in 10 ml. water and 1.5 ml. of ethanol was refluxed for 30 min., a homogeneous solution having been formed within 15 min. Ethanol was driven off and the mixture was cooled and acidified to give a semi-solid product which was taken up in chloroform and extracted twice with a cold saturated solution of sodium bicarbonate. The bicarbonate layer was washed with chloroform, cooled, and cautiously acidified when a semi-solid product separated. This was extracted with chloroform and the chloroform layer washed, dried and freed from solvents to give 0.5 g. of a colorless viscous oil which was crystallized from 10 ml. of petroleum ether (30–60°) to give small flat needles of the α,β-unsaturated keto acid VIIa, 0.3 g., m.p. 60–63°. Repeated crystallizations from aqueous methanol and petroleum ether raised the m.p. to 74–75°, $[\alpha]^{23}D$ −154.4° (95% ethanol, *c* 0.56); infrared bands at 3500 (acid -OH), 3000–3500 (broad, bonded acid -OH), 1745 (monomeric carboxyl), 1700 (carboxyl), 1660 (cycloheptenone) and 1630 cm.$^{-1}$ (C=C). The ultraviolet spectrum (isoöctane) exhibited a maximum at 235 mμ (ϵ 3696).

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.05; H, 8.41.

Treatment of Dehydrodesoxoepitetrahydrohelenalin with Sodium Carbonate.—A mixture of 120 mg. of VIc, 250 mg. of sodium carbonate, 0.5 ml. of ethanol and 3 ml. of water was refluxed for 1.5 hr. until a homogeneous solution was obtained. Ethanol was driven off, the reaction mixture was cooled and acidified to give an oil which was extracted with chloroform. The chloroform layer was extracted with dilute aqueous sodium bicarbonate and the bicarbonate layer was washed with chloroform, cooled and acidified to give an oil. Extraction with chloroform, washing the extract with water, drying, and removal of solvent left behind 60 mg. of a viscous oil which solidified on standing. Crystallization from aqueous methanol gave 30 mg. of colorless thick needles, m.p. 124.5–125°. A mixed m.p. with an authentic sample of VIIb, m.p. 125–126°, obtained from dehydrodesoxodesacetyldihydroalloisotenulin,[4] was 124–125°. The infrared spectra of the two were identical. For comparison with VIIa, the ultraviolet spectrum of VIIb, previously[4] reported in ethanol, was determined in isoöctane, λ_{max} 230 mμ (ϵ 5582) (experiment by Mr. W. A. Rohde). It is not clear as yet whether the difference in λ_{max} and ϵ is due to *cis-trans* isomerism or *endo-exo* migration of the double bond.

Lithium Aluminum Hydride Reduction of Desoxoepitetrahydrohelenalin.—The reduction of 200 mg. of VIc with 150 mg. of lithium aluminum hydride in 200 ml. of anhydrous ether was carried out in a Soxhlet extractor with the solid hydroxylactone placed in the thimble. After 36 hr. of refluxing the reaction mixture was treated with moist ether, then cautiously with water and finally acidified with 10 ml. of 10% sulfuric acid. The clear ether layer was washed acid-free, dried and freed from solvent to give 190 mg. of a clean viscous oily triol. Attempts to crystallize the triol were unsuccessful. Purification by distillation *in vacuo* gave a colorless viscous oil, b.p. 157–160° (bath temp., 0.02 mm.), $[\alpha]^{25}D$ −27.4° (95% ethanol, *c* 0.53), infrared bands at 3590 (free -OH) and 3390 cm.$^{-1}$ (bonded -OH).

Anal. Calcd. for $C_{15}H_{28}O_3$: C, 70.27; H, 11.01. Found: C, 70.80; H, 10.74.

Lithium Aluminum Hydride Reduction of Desoxotetrahydrohelenalin.—A solution of 120 mg. of VIa in 70 ml. of dry ether was treated with 100 mg. of lithium aluminum hydride and the mixture refluxed for 24 hr. Working up in the usual manner furnished 120 mg. of the triol as a colorless viscous oil. This was shown to be identical with the triol described in the preceding paragraph through its rotation and infrared spectrum.

Treatment of Tetrahydrohelenalin with Raney Nickel.—A solution of 50 mg. of tetrahydrohelenalin in 15 ml. of absolute ethanol was refluxed with 0.5 g. of Raney nickel for 19 hr. The nickel was removed and the solvent evaporated to dryness to give an oily residue which solidifies on standing. Crystallization from aqueous ethanol gave 35 mg. of fine needles, m.p. 166–168°. A mixed m.p. with a sample of authentic tetrahydrohelenalin, m.p. 171–173°, was 168–169°.

Treatment of Tetrahydrohelenalin with BF_3 Etherate.—A mixture of 50 mg. of tetrahydrohelenalin and 0.5 ml. of BF_3-etherate was allowed to stand for 45 minutes and then diluted with water and extracted with benzene. The benzene layer was washed acid-free, dried and freed of solvents to give a crystalline residue which was recrystallized from aqueous ethanol to give fine needles, m.p. 170–172°, undepressed when mixed with an authentic specimen of tetrahydrohelenalin, m.p. 171–173°.

Chromatography of tetrahydrohelenalin in benzene over basic alumina gave unchanged starting material in quantitative yields.

TALLAHASSEE, FLA.