anisaldehyde and *p*-hydroxybenzaldehyde are essentially identical (Table I), as are those of anisole and phenol.[18]

**Enzymatic Synthesis of *p*-Hydroxybenzyl β-D-Glucopyranoside and *o*-Hydroxybenzyl β-D-Glucopyranoside.**—The enzymatic synthesis of *o*-hydroxybenzyl β-D-glucoside was reported many years ago by Bourquelot and Hérissey.[19] *p*-Hydroxybenzyl β-D-glucoside has not been synthesized before, but since it is very similar in structure to the *o*-hydroxybenzyl derivative the procedure of Bourquelot and Hérissey was tried. Following their directions, 25 g. of *o*-hydroxybenzyl alcohol, 2 g. of glucose, and 1 g. of emulsin were dissolved in a mixture of 20 ml. of water and 70 ml. of acetone, and the mixture was incubated at 15–20° for 19 days with occasional shaking. The same reaction mixture was used for *p*-hydroxybenzyl glucoside, except that the amount of acetone was increased to 100 ml. because of the lower solubility of *p*-hydroxybenzyl alcohol. When incubation was complete, the mixtures were filtered, and the filtrates were evaporated to sirup in a rotary vacuum evaporator. The sirups were dissolved in 30 ml. of water and extracted with ether to remove the unreacted alcohols. After aeration to remove ether, each solution was incubated with 3 g. of starch-free baker's yeast at 37° until no free glucose could be detected by glucose oxidase paper (Tes-tap, Eli Lilly Co.). The yeast was then filtered off, and the filtrates were decolorized with active carbon.

Portions of the decolorized solutions were streaked on Whatman No. 3 papers, which were then irrigated with 1-butanol–ethanol–water 40:11:19. Two pilot strips were cut from each chromatogram. One strip was sprayed with ammoniacal silver nitrate to detect glucosides and the other with diazotized *p*-nitroaniline–sodium carbonate reagent[20] to detect phenolic compounds. The *o*-hydroxybenzyl alcohol reaction mixture gave five bands positive to ammoniacal silver nitrate, and the *p*-hydroxybenzyl alcohol mixture four, but only one band from each mixture gave color with diazotized *p*-nitroaniline. The bands positive to both spray reagents were cut out and eluted with water, and the concentration of glucoside in the eluates was determined by the anthrone method.[21]

Ramart-Lucas and Rabaté[18] reported that the ultraviolet absorption spectrum of *o*-hydroxybenzyl β-D-glucoside was identical with that of its aglycone, *o*-hydroxybenzyl alcohol. The eluted substances could thus be characterized as the desired hydroxybenzyl glucosides by their ultraviolet spectra, which were examined in both acidic and alkaline solutions. It was found (Table I) that in both cases the spectra were identical, in $\lambda_{max}$ as well as $A_m$, with those of the respective hydroxybenzyl alcohols. It was estimated that 0.27 g. of *o*-hydroxybenzyl β-D-glucoside and 0.18 g. of *p*-hydroxybenzyl β-D-glucoside were synthesized in these operations.

**Alkaline Methanolysis.**—To 4.4 mg. of dhurrin in 10 ml. of dry methanol was added 1.3 ml. of 1.44 *N* barium methoxide. After 2 hr. at room temperature, the reaction was stopped by carbonation with $CO_2$ gas. Barium carbonate was removed by filtration and the filtrate was concentrated to 3 ml. in a rotary vacuum evaporator. A gummy precipitate formed in the concentrate during a 0.5 hr. standing. This precipitate was filtered off and the clear filtrate was used for paper chromatographic analysis (Whatman No. 1 paper, 1-butanol–ethanol–water 40:11:19, visualization with ammoniacal silver nitrate).

**$R_f$ Values.**—The $R_f$ values, in 1-butanol–ethanol–water 40:11:19, of the glucosides and sugars separated or identified by paper chromatography in the present work are listed here for convenience.

| | |
|---|---|
| D-Glucose | 0.24 |
| D-Fructose | 0.28 |
| Methyl α-D-glucopyranoside | 0.37 |
| Dhurrin | 0.72 |
| *p*-Methoxymandelonitrile β-D-glucopyranoside | 0.88 |
| *o*-Hydroxybenzyl β-D-glucopyranoside | 0.70 |
| *p*-Hydroxybenzyl β-D-glucopyranoside | 0.62 |

(19) E. Bourquelot and H. Hérissey, *J. pharm. chim.*, *Ser. 7*, **8**, 49 (1913).
(20) T. Swain, *Biochem. J.*, **53**, 200 (1953).
(21) D. L. Morris, *Science*, **107**, 254 (1948).

# The Constituents of *Ecballium elaterium* L. XXI.[1,2] Isomerism in Ring A of the Cucurbitanes

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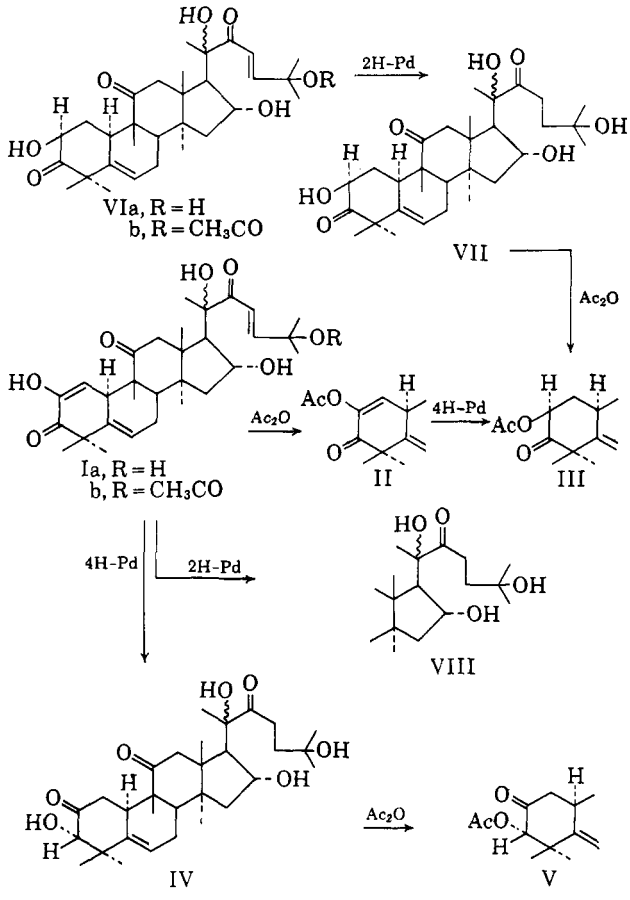
*Received August 11, 1964*

New evidence shows that the hydrogenation of the diosphenol-containing elatericin B (Ia) proceeds through a 1,4-addition of hydrogen to yield tetrahydroisoelatericin B (3-hydroxy-2-one), whereas the acetoxy derivative (II) proceeds through a 1,2-addition yielding a 2-acetoxy-3-one product (III).

In previous papers dealing with the hydrogenation of the diosphenol-containing cucurbitacins, namely elatericin B (Ia) and elaterin (Ib) it has been reported that the first mole of hydrogen was consumed in the reduction of the double bond on the side chain, whereas the second reduced the enolic double bond of the diosphenol system in ring A.[4] It was expected that products identical with dihydroelatericin A (VII) or dihydrocucurbitacin B (23,24-dihydro VIb) should form. However, different compounds were obtained. The difference was explained in terms of the formation of epimers involving the center of asymmetry at C-2. These conclusions were made on the basis of infrared and ultraviolet spectroscopy as well as optical rotatory dispersion measurements.[4] The n.m.r. spectrum of the hydrogenation product of elatericin B was now found to show a singlet at $\tau$ 6.02 and that of its diacetate, a sharp one at $\tau$ 5.0. This observation clearly points to the fact that the proton linked to the carbon to which the acetoxy group is also attached has *no neighboring protons* and cannot, therefore, be at the formerly assumed C-2 position. The latter would have displayed of necessity a multiplet due to spin–spin coupling with the adjacent hydrogens at C-1. In order to account for the singlet in the n.m.r. spectrum, the alternate C-3 position for the hydrogen in question had to be considered through a possible 1,4-addition of hydrogen to the diosphenol system, resulting in the conversion of the $\Delta^1$-2-hydroxy-3-keto to a 2-keto-3-hydroxy system which we now call tetrahydroisoelatericin B (IV). In this compound the acetoxy group has probably the most stable α-equatorial orientation.

(1) This investigation was supported by a research grant, CA-2810, from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.
(2) Part XX: D. Lavie and B. S. Benjaminov, *Tetrahedron*, **20**, 2665 (1964).
(3) This author gratefully acknowledges the National Cancer Institute Fellowship (CA-19,319) of the National Institutes of Health, U. S. Public Health Service, and the leave of absence from Rose Polytechnic Institute, Terre Haute, Ind.
(4) D. Lavie, Y. Shvo, O. R. Gottlieb, and E. Glotter, *J. Org. Chem.*, **28**, 1790 (1963), and the references cited therein.




Upon hydrogenating elatericin B diacetate (II), however, a normal 1,2-addition takes place resulting in the formation of the 2-acetoxy-3-keto derivative, tetrahydroelatericin B diacetate (III), which points to a $\beta$-equatorial orientation for the 2-acetoxy group. Indeed, one can distinctly observe a quartet of lines related to the 2,$\alpha$-axial proton which is centered at $\tau$ 4.4 ($J_{aa}$ = 13.5 c.p.s.; $J_{ae}$ = 5.1 c.p.s.). Tetrahydroelatericin B diacetate (III) was found to be identical in all respects with dihydroelatericin A diacetate (III) which was obtained by the acetylation of dihydroelatericin A (VII).[5] These two compounds could not be induced to crystallize, but both displayed identical infrared and n.m.r. spectra throughout the entire range, and both had similar $R_f$ values on a chromatoplate.

In view of previous hydrogenation experiments leading to similar results in the euphol series, in which it had been observed that the 2-acetoxy-3-keto derivative isomerizes rather easily to the 2-keto-3-acetoxy compound,[6] tetrahydroelatericin B diacetate, III (as well as the similar dihydroelatericin A diacetate obtained by the acetylation of dihydroelatericin A, VII) was allowed to stand on a column packed with activated basic alumina in order to induce isomerization. Examination of the material recovered from the column showed that it had remained unchanged. The same was true when acid-washed alumina was used. It may be concluded, therefore, that no isomerization occurs in the case of elatericin A or its acetate and that the apparent isomer formation during the hydrogenation of elatericin B is entirely attributable to a 1,4-addition. A further contributing factor here is the fact that, while in euphol there is a $\beta$-oriented methyl group at C-10 which is engaged in a 1,3-diaxial interaction, in the cucurbitacins there is an $\alpha$-oriented hydrogen at this same location and hence isomerization does not lead to release of strain in ring A.

While the n.m.r. measurements made it possible to establish the structural differences existing between dihydroelatericin A (VII) and tetrahydroisoelatericin B (IV), the optical rotatory dispersion data had to be interpreted. The Cotton effect of 2- and 3-keto steroids was found to be positive, although the amplitude of the latter is smaller.[7] The same is true of the oxomanoyl oxide series and the same regularities are therefore applicable to the 4,4-dimethyl terpene series; the Cotton effect of both 2- and 3-keto oxomanoyl derivative is positive with the amplitude[8] of the 2-keto derivative being about three times as large as that of the 3-keto form.

In the cucurbitacin series one should take into consideration the effect of the inverted stereochemistry at C-10 resulting in a mirror image of the C-10, $\beta$-analog and therefore their optical rotatory dispersion curve should be inverted. Indeed, in dihydroelatericin A (VII) (3-keto) the peak, $[\alpha]_{325}$ +2200°, is larger than that of tetrahydroisoelatericin B (IV) (2-keto),[4] $[\alpha]_{325}$ +1550°. In both cases the keto group is flanked by an equatorial OH substituent which is either likely to increase the Cotton effect or to render no change at all.

In following this line of reasoning it should be mentioned that, instead of negative Cotton effects, the two cucurbitacins displayed positive curves. This can be easily understood by taking into consideration the presence of two additional carbonyl chromophores, one in particular at C-11 displaying a large amplitude[4] which counteracts thereby the inverted rotation of the keto groups in ring A as should be expected. The result is a lower positive peak value instead of a negative one.

The alkaline hydrolysis in ethanol of tetrahydroelatericin B diacetate (III) was carried out in order to obtain pure tetrahydroelatericin B (same as dihydroelatericin A, VII). However, the reaction consistently resulted in the formation of dihydroelatericin B (VIII).[9] In order to verify the time factor involved, the hydrolysis was carried out for varying lengths of time. Samples were checked spectroscopically every half hour. The third sample (1.5 hr.) showed distinctly the disappearance of the acetate bands in the infrared which were still present in the 1-hr. sample, while the ultraviolet spectrum showed a peak at $\lambda_{max}$ 267 m$\mu$ ($\epsilon$ 5700).[10] The latter, which is characteristic of the diosphenol system as present in dihydroelatericin B (VIII), remained almost unchanged in all following samples. The third sample gave a positive ferric chloride test. When the reaction was conducted in a methanolic solution an acceleration in the hydrolysis was observed and the diosphenol was formed within a half hour. However, repeating this experiment at

(5) A similar pattern of signals for elatericin A diacetate has been described in ref. 4.

(6) D. Lavie, E. Glotter, and Y. Shvo, *Tetrahedron*, **19**, 1377 (1963).

(7) C. Djerassi, O. Halpern, V. Halpern, and B. Riniker, *J. Am. Chem. Soc.*, **80**, 4001 (1958).

(8) C. Djerassi and W. Klyne, *J. Chem. Soc.*, 4929 (1962).

(9) D. Lavie and D. Willner, *J. Am. Chem. Soc.*, **80**, 710 (1958).

(10) D. Lavie and S. Szinai, *ibid.*, **80**, 707 (1958).

pH 9 it was found that this time the hydrolysis product was identical with dihydroelatericin A (VII) when checked on a chromatoplate. No absorption maximum in the ultraviolet spectrum was recorded (only end absorption).

Furthermore, even when tetrahydroisoelatericin B diacetate (V) was subjected to alkaline hydrolytic conditions, dihydroelatericin B (VIII) was formed as indicated by the appearance of the typical enolate ion [$\lambda_{max}$ 310 m$\mu$ ($\epsilon$ 5000)].[10]

The alkali-induced autoxidation of the $\alpha$-hydroxy ketone in elatericin A (VI) has been previously reported[11] and was found to occur at a much slower rate than the same reaction now involving the acetate derivatives. Carrying out the experiment under nitrogen did not appreciably effect the reaction. Experiments dealing with dihydrocucurbitacin B (23,24-dihydro VIb) and its diacetate[12] led to similar results. Furthermore, acid treatment (HCl) of tetrahydroelatericin B diacetate (III) led only to partial hydrolysis.

The new evidence which we are reporting here clarifies the hydrogenation of diosphenol-containing cucurbitacins, something that has been a matter of controversy in previous publications.[4] An early observation[13] pointed out that when the hydrogenation was performed on the diosphenol acetate II (of elatericin B Ia and of elaterin Ib), a product was obtained which proved common to the one obtained through an alternate scheme starting with the diacetates of elatericin A (VIa) and cucurbitacin B (VIb), both having a 2-acetoxy-3-keto system in ring A (see flow chart in ref. 13). Later publications,[4] however, dealing with the hydrogenation of the diosphenol-containing compounds, described erroneously the formation of 2-hydroxy-3-keto derivatives epimeric at C-2 with the naturally occurring 2-hydroxy-3-keto compounds, namely elatericin A (VIa) and cucurbitacin B (VIb). The respective acetates were also found to be different. This discrepancy is now straightened in view of the present observation that while the hydrogenation of the diosphenol acetate yields a 2-acetoxy-3-keto compound, that of the diosphenol itself results in a 2-keto-3-hydroxy compound and the corresponding 3-acetoxy after acetylation.

## Experimental

Melting points were taken on a Kofler hot-stage microscope and are corrected. All optical rotation measurements were carried out in chloroform solution. Ultraviolet absorption spectra were done on a Cary 14 spectrophotometer in ethanol solution. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137 spectrometer equipped with a sodium chloride prism and, unless otherwise stated, were determined in chloroform solution in 5–10% concentration. N.m.r. spectra were recorded on a Varian A-60 spectrometer. The spectra were determined in deuterated chloroform solutions of about 5–10% concentration and contained tetramethylsilane as internal standard; the line positions given are $\tau$-values. Thin layer chromatography was done on chromatoplates of silica gel G (Merck) and spots were developed with potassium permanganate, 0.5% solution in a saturated cupric acetate solution.

**Hydrogenation of Elatericin B (I) to Tetrahydroisoelatericin B (IV).**[9,14]—Elatericin B (500 mg.) in ethanol (50 ml.) was hydrogenated as reported over 10% palladium on charcoal (50 mg.) at atmospheric pressure (54 ml. of hydrogen absorbed). The residue (480 mg.) gave a negative ferric chloride test and showed three spots on the chromatoplate. The product IV (480 mg.) was chromatographed through a column packed with acid-washed alumina (48 g.). Elution with methanol–chloroform (2:98) yielded crystalline fractions which showed one spot on a chromatoplate (ethyl acetate–benzene, 8:2). The product was recrystallized from ether–methanol: m.p. 173–176°; $[\alpha]_D$ +59° (*c* 0.88); $\nu_{max}$ 1706 (broad band) and 1698 cm.$^{-1}$ (C-11 carbonyl group); ultraviolet end absorption.

*Anal.* Calcd. for $C_{30}H_{48}O_7$: C, 69.20; H, 9.29. Found: C, 68.90; H, 9.45.

**Acetylation of Tetrahydroisoelatericin B (IV) to Tetrahydroisoelatericin B Diacetate (V).**[14]—Tetrahydroisoelatericin B (IV, 200 mg.) was acetylated at room temperature overnight in pyridine (4 ml.) and acetic anhydride (4 ml.). Ice was added and the amorphous solid was extracted with chloroform. The chloroform solution was washed with dilute HCl, 10% aqueous sodium bicarbonate solution, and water, then dried over sodium sulfate. The product (V, 180 mg.) produced a single spot on a chromatoplate (ethyl acetate–benzene, 8:2) and gave a negative ferric chloride test: $\nu_{max}$ 1739, 1698, and 1235 cm.$^{-1}$; ultraviolet end absorption; n.m.r., sharp singlet at $\tau$ 5.0, unresolved peak at 4.0 (C-6, vinylic proton), and triplet centered at 4.8 (C-16 proton).

*Anal.* Calcd. for $C_{34}H_{52}O_9$: C, 67.75; H, 8.36; $2CH_3CO$, 14.28. Found: C, 67.21; H, 8.38; $CH_3CO$, 14.92.

**Elatericin B diacetate (II) from elatericin B (I),** prepared as previously described,[15] showed a single spot on a chromatoplate (ethyl acetate–benzene, 8:2): m.p. 249–251° dec.; $[\alpha]_D$ −82° (*c* 1.52); $\nu_{max}$ 1767 (enol acetate), 1739 (acetate), 1701 (overlapping of C-11 and C-22 carbonyl groups), 1634 ($\Delta^1$), and 1202 (enol acetate) cm.$^{-1}$.

**Tetrahydroelatericin B Diacetate (III) from Elatericin B Diacetate (II).**—Elatericin B diacetate (II, 1.2 g.) in ethanol (50 ml.) was hydrogenated over 10% palladium on charcoal (100 mg.) at atmospheric pressure until about 99 ml. of hydrogen had been absorbed, and the procedure described above was followed. The residue (III, 1.02 g.) gave a negative ferric chloride test and one spot on the chromatoplate (ethyl acetate–benzene, 8:2): $[\alpha]_D$ −11° (*c* 1.10); $\nu_{max}$ 1739, 1704, and 1233 cm.$^{-1}$; ultraviolet end absorption; n.m.r. quartet centered at $\tau$ 4.4 ($J_{ae}$ = 5.1 c.p.s., $J_{aa}$ = 13.5 c.p.s.), 4.06 (C-6 vinylic proton), and triplet centered at 4.8 (C-16 proton).

**Dihydroelatericin A Diacetate (III) from Dihydroelatericin A (VII).**—Prepared as previously described,[4] it produced a single spot on the chromatoplate (ethyl acetate–benzene, 8:2): $[\alpha]_D$ −11° (*c* 1.16); n.m.r. quartet centered at $\tau$ 4.4 ($J_{ae}$ = 5.1 c.p.s., $J_{aa}$ = 13.5 c.p.s.), 4.08 (C-6 vinylic proton), and triplet centered at 4.73 (C-16 proton); identical infrared spectra with tetrahydroelatericin B diacetate (III).

**Attempt to Isomerize Dihydroelatericin A Diacetate or Tetrahydroelatericin B Diacetate (III).**—A sample each of dihydroelatericin A diacetate (III, 100 mg.) and tetrahydroelatericin B diacetate dissolved in benzene was adsorbed on a column packed with activated basic alumina (Alcoa F20, 20 g.) and allowed to stand 24 hr. Elution with benzene yielded the starting material unchanged.

**Hydrolysis of Tetrahydroelatericin B Diacetate (III). A. Alkaline Hydrolysis in Ethanol.**—A sample of tetrahydroelatericin B diacetate (III, 500 mg.) was dissolved in ethanol (100 ml.) and divided into five aliquots. To each 5 ml. of a 4% aqueous sodium hydroxide solution was added to produce 25 ml. (0.2 *N* solution). The five alkaline samples were allowed to stand for 0.5, 1, 1.5, 2, and 2.5 hr., respectively, and then each was made neutral and evaporated to a small volume. Water was next added and the hydrolysis product was extracted with chloroform, washed with water, dried over sodium sulfate, and evaporated to dryness. The residue of each sample was checked for ferric chloride test and pertinent infrared and ultraviolet spectra are given: after 1 hr.—$\nu_{max}$ 1739, 1704, and 1236 cm.$^{-1}$; ultraviolet end absorption; negative ferric chloride test; and, after 1.5 hr.—$\nu_{max}$ 1692, 1661, and 1400 cm.$^{-1}$; $\lambda_{max}$ 267 m$\mu$ ($\epsilon$ 5700); positive ferric chloride test.

(11) D. Lavie and Y. Shvo, *J. Am. Chem. Soc.*, **81**, 3058 (1959).

(12) W. Schlegel and C. R. Noller, *J. Org. Chem.*, **26**, 1211 (1961); A. Melera and C. R. Noller, *ibid.*, **26**, 1213 (1961).

(13) D. Lavie, Y. Shvo, D. Willner, P. R. Enslin, J. M. Hugo, and K. B. Norton, *Chem. Ind.* (London), 951 (1959).

(14) *Cf.* O. R. Gottlieb and D. Lavie, *Anais assoc. brasil. quim.*, **19**, 185 (1960).

(15) D. Lavie and Y. Shvo, *J. Am. Chem. Soc.*, **82**, 966 (1960).

**B. Alkaline Hydrolysis in Methanol.**—Tetrahydroelatericin B diacetate (III, 500 mg.) was dissolved in methanol (100 ml.) and treated with aqueous sodium hydroxide as above: after 0.5 hr.—$\nu_{max}$ 1705, 1692, 1660, and 1410 cm.$^{-1}$; $\lambda_{max}$ 268 m$\mu$ ($\epsilon$ 4900); positive ferric chloride.

**C. Hydrolysis in Methanol at pH 9.**—Tetrahydroelatericin B diacetate (III, 60 mg.) was dissolved in methanol (30 ml.) and 4% aqueous sodium hydroxide solution was added to pH 9. The alkaline methanolic solution of III was allowed to stand for 5 hr., then treated as above. The residue (50 mg.) produced one major spot on a chromatoplate: $\nu_{max}$ 1704 (broad), 1672 (very weak), and 1264 cm.$^{-1}$; slightly positive ferric chloride test.

**Acknowledgment.**—We thank Dr. Y. Shvo for the n.m.r. measurements and for contributing to their interpretation. We also thank Mrs. R. Lazar for technical assistance.

# *Helichrysum* Seed Oil. II. Structure and Chemistry of a New Enynolic Acid[1]

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*Received September 14, 1964*

Helenynolic acid, a new hydroxy acid isolated from *Helichrysum bracteatum* seed oil, is shown to have the structure 9-hydroxy-*trans*-10-octadecen-12-ynoic acid (Ia) by oxidative degradation, spectral properties, and lithium aluminum hydride reduction. This acid is resistant to acid-catalyzed dehydration, but undergoes etherification in acidic methanol with considerable facility.

The isolation of a new hydroxy acid having a conjugated enyne grouping was described in part I of this series.[3] This acid was found as one of several unusual triglyceride substituents in *Helichrysum bracteatum* seed oil. This present paper deals with the proof of structure of this new acid and some of its chemistry.

The pure methyl ester of helenynolic acid (Ib) had absorption maxima at 4.54 and 10.46 $\mu$ in its infrared spectrum (see Figure 1), and at 228 m$\mu$ in its ultraviolet

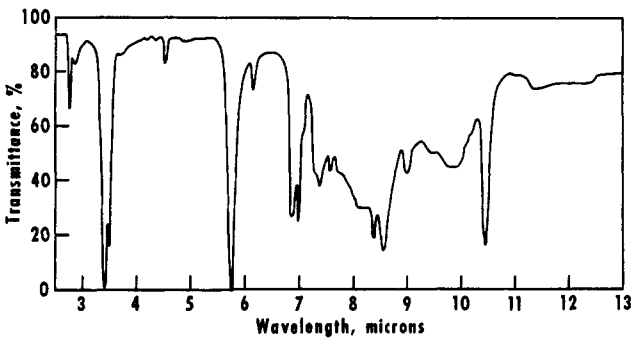


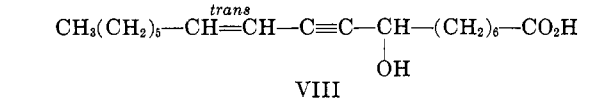

Figure 1.—Infrared spectrum of methyl helenynolate (Ib).

spectrum, that indicated a conjugated *trans*-enyne chromophore.[4,5] Ib was also indicated to be a monohydroxy ester by an infrared maximum of moderate intensity in the OH region (2.77 $\mu$). It was found to be slightly levorotatory.

Hydrogenation of Ib with Adams catalyst in ethanol did not give satisfactory results. The desired product II, the saturated hydroxy ester corresponding to Ib, was formed in poor yield (50%). It was accompanied by a considerable amount (45%) of hydrogenolysis product (methyl stearate) and small amounts of keto ester as well as other minor components. II was obtained in much better yield (80%) by hydrogenating Ib in acetic acid solution with palladium–charcoal catalyst. Formation of keto esters by double-bond migration during hydrogenation had been observed previously.[6] Equally contrasting results in the use of platinum and palladium catalysts for hydrogenating compounds with activated hydroxyl groups was observed in work on oenanthotoxin and cicutoxin.[7] Similar hydrogenolyses of activated hydroxyls in acetylenic acids in isano oil[8] and in methyl dimorphecolate[9a] also have been reported. Results obtained on hydrogenating Ib with a rhodium–alumina catalyst in acetic acid[9b] were comparable with those obtained with palladium–charcoal. Ib consumed 3.25 moles of hydrogen in the presence of the rhodium–alumina catalyst.

The structure of saturated hydroxy ester II was established by oxidative cleavage with chromium trioxide in acetic acid. The cleavage products obtained, nonanoic and decanoic acids in nearly equal amounts together with half esters of octanedioic and nonanedioic acids in nearly equal amounts, placed the hydroxyl at C-9 on a normal $C_{18}$ skeleton. (See Chart I.)

Permanganate–periodate cleavage of methyl helenynolate (Ib) yielded hexanoic acid and nonanedioic acid half ester. This result indicated that the enyne grouping and the hydroxyl group were located between C-9 and C-13, and suggested that helenynolic acid was closely analogous to 8-hydroxyimenynic (8-hydroxy-*trans*-11-octadecen-9-ynoic) acid (VIII). The latter acid, a constituent of *Ximenia caffra* kernel oil, was characterized by Ligthelm[10] and later synthesized by Crombie and Griffin.[11] However, lithium aluminum hydride reduction of Ib demonstrated that it was not an analog of VIII. Ligthelm[10] obtained *trans*-9,*trans*-




VIII

(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article is not copyrighted.

(3) R. G. Powell, C. R. Smith, Jr., and I. A. Wolff, *J. Am. Oil Chemists' Soc.*, submitted for publication.

(4) S. P. Ligthelm, H. M. Schwartz, and M. M. von Holdt, *J. Chem. Soc.*, 1088 (1952).

(5) L. Crombie and A. G. Jacklin, *ibid.*, 1622 (1957).

(6) T. H. Applewhite, M. J. Diamond, and L. A. Goldblatt, *J. Am. Oil Chemists' Soc.*, **38**, 609 (1961).

(7) E. F. L. J. Anet, B. Lythgoe, M. H. Silk, and S. Trippett, *J. Chem. Soc.*, 309 (1953).

(8) F. D. Gunstone and A. J. Sealy, *ibid.*, 5772 (1963).

(9) (a) C. R. Smith, Jr., T. L. Wilson, E. H. Melvin, and I. A. Wolff, *J. Am. Chem. Soc.*, **76**, 1417 (1960); (b) T. H. Applewhite, personal communication.

(10) S. P. Ligthelm, *Chem. Ind.* (London), 249 (1954).

(11) L. Crombie and B. P. Griffin, *J. Chem. Soc.*, 4435 (1958).