tracted with chloroform and worked up in the usual fashion. The residual gum, 19.2 g. was chromatographed over 160 g. of silicic acid. The column was eluted with benzene, benzene–chloroform, chloroform, and chloroform–methanol, but none of the eluates furnished crystalline material.

Optical Rotatory Dispersion and Absolute Configuration. VI. Structure and Absolute Configuration of Helenynolic Acid[1]

J. Cymerman Craig, S. K. Roy,

Department of Pharmaceutical Chemistry,
University of California, San Francisco, California 94122

R. G. Powell, and C. R. Smith, Jr.

Northern Regional Research Laboratory,[2]
Peoria, Illinois 61604

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Helenynolic acid, a new hydroxy acid containing the vinylacetylene chromophore, was recently isolated from the seed oil of *Helichrysum bracteatum* and was shown[3] by oxidative degradation, spectral properties, and lithium aluminum hydride reduction to have the structure 9-hydroxy-*trans*-10-octadecen-12-ynoic acid (Ia). It is thus closely related to 8-hydroxyximenynic acid (II), 8-hydroxyisanic acid (III), and 8-hydroxybolekic acid (IV), all of which occur in natural fats and oils and possess the normal C_{18} skeleton.[4]

$$CH_3(CH_2)_4C{\equiv}CCH{=}CHCH(OH)(CH_2)_7COOR$$

Ia, R = H
b, R = CH_3

$$CH_3(CH_2)_5CH{=}CHC{\equiv}CCH(OH)(CH_2)_6COOH$$

II

$$CH_2{=}CH(CH_2)_4(C{\equiv}C)_2CH(OH)(CH_2)_6COOH$$

III

$$CH_2{=}CH(CH_2)_2CH{=}CH(C{\equiv}C)_2CH(OH)(CH_2)_6COOH$$

IV

The absolute configuration of the asymmetric carbon atom in I is of considerable interest in view of current work[4] on the biogenesis of the C_{18} acetylenic acids in plants.

The rotatory dispersion curve of methyl helenynolate (Figure 1) shows two closely spaced positive Cotton effects, with peaks at 232 and 243 mμ, superimposed on a strong positive background. This is in excellent agreement with its vinylacetylene chromophore [λ_{max} 228 and 238 mμ (ε 17,400 and 14,300, respectively)].

Hydrogenation of methyl helenynolate with 10% palladium on charcoal in methanol gave a saturated ester, m.p. 51°, identified as methyl 9-D-hydroxyoctadecanoate by comparison with a sample prepared by the action of diazomethane on synthetic 9-D-hydroxyoctadecanoic acid.[5] The identity of the natural and the synthetic samples by mixture melting point, infrared spectrum, and gas chromatographic retention time offers conclusive proof of the correct location of the 9-hydroxy group in I.

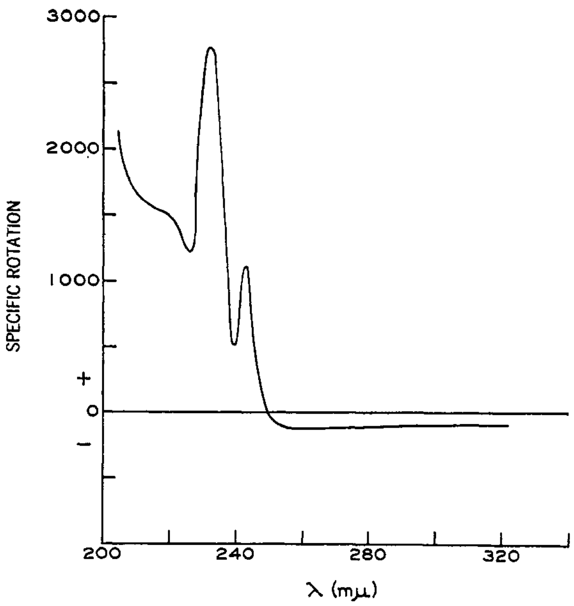

Figure 1.—Rotatory dispersion curve of (−)-methyl helenynolate.

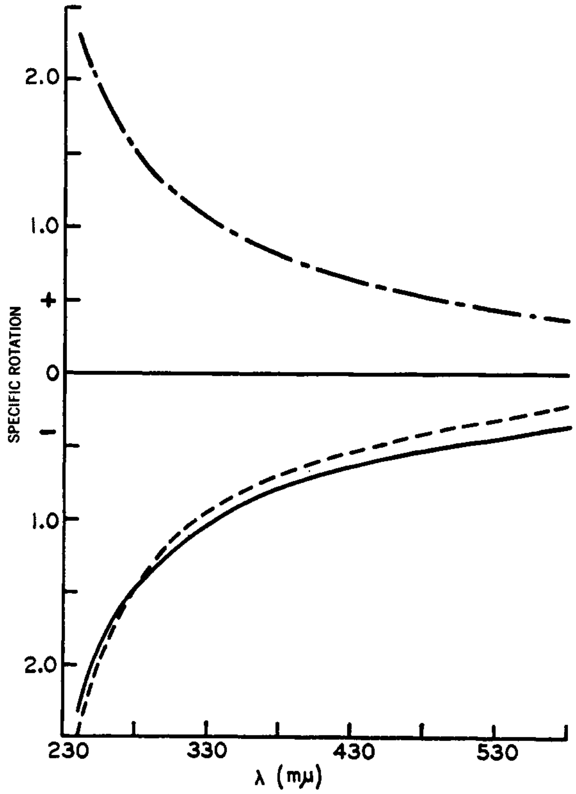

Figure 2.—Rotatory dispersion curves of (−)-methyl 12-D-hydroxyoctadecanoate (———), (+)-methyl 12-L-hydroxyoctadecanoate (—·—·), and (−)-methyl 9-D-hydroxyoctadecanoate (– – –).

The two samples of the ester also gave the same rotatory dispersion curve (Figure 2), closely similar to that (Figure 2) of (−)-methyl 12-D-hydroxyoctadecanoate, obtained from D-(+)-methyl ricinoleate by catalytic hydrogenation. Since both ricinoleic acid and its hydrogenation product (−)-12-hydroxyoctadecanoic

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[2] A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] R. G. Powell, C. R. Smith, Jr., C. A. Glass, and I. A. Wolff, *J. Org. Chem.*, **30**, 610 (1965).

[4] For review, see J. D. Bu'Lock, *Progr. Org. Chem.*, **6**, 86 (1964).

[5] C. D. Baker and F. D. Gunstone, *J. Chem. Soc.*, 759 (1963). We are indebted to Professor Gunstone for a sample of synthetic 9-D-hydroxyoctadecanoic acid.

acid have been shown[6] to possess the D configuration, the results in Figure 2 also confirm the correctness of the D configuration deduced[5,7] for natural 9-hydroxy-12-octadecenoic acid and the derived 9-hydroxyoctadecanoic acid on the basis of mixture melting point data. The D configuration may now similarly be assigned to natural helenynolic acid (I).[8]

In order to furnish proof of the validity of the rotatory dispersion curves in Figure 2, (−)-methyl-12-D-hydroxyoctadecanoate was inverted by formation of the tosylate, conversion of this to the acetate, and mild hydrolysis of the latter to yield the enantiomeric (+)-methyl 12-L-hydroxyoctadecanoate, using an adaptation of the method of Schroepfer and Bloch.[10] The L-(+) ester [identical with its D-(−) isomer in melting point and infrared spectrum] is seen (Figure 2) to have a rotatory dispersion curve which is the exact mirror image of that of the D-(−) compound.

Experimental Section[11]

Rotatory dispersion curves were determined with a Bendix Model 460-C or a Cary Model 60 spectropolarimeter using 1-mm. or 1-cm. cells (*c* 0.06–6.0, 95% ethanol) at 25°. Rotations are given below only for (1) the highest and lowest wave lengths measured, and (2) peaks and troughs. Results were reproducible to within 5%.

Methyl helenynolate had $[\alpha]_{600}$ −7° (*c* 3.6, ethanol); O.R.D. (*c* 0.06, ethanol) $[\alpha]_{323}$ −75.5°, $[\alpha]_{243.5}$ 1115° (peak), $[\alpha]_{240}$ 512° (trough), $[\alpha]_{232.5}$ 2795° (peak), $[\alpha]_{226}$ 1241° (trough), $[\alpha]_{204}$ 2150°.

Hydrogenation of Methyl Helenynolate.—A solution of 30 mg. of the acetylenic ester in 10 ml. of methanol was hydrogenated in presence of 60 mg. of 10% palladium on charcoal at 15 p.s.i. and room temperature for 1 hr. Filtration and evaporation under reduced pressure gave a white solid, m.p. 45–50°, which was chromatographed on silicic acid (activated by heating to 90° for 24 hr.). The fraction eluted with pentane–ether (9:1) gave 24 mg. (80% yield) of methyl 9-hydroxyoctadecanoate, m.p. 50–51° (*Anal.* Calcd. for $C_{19}H_{38}O_3 \cdot 0.25H_2O$: C, 71.54; H, 12.16. Found: C, 71.55, 71.57; H, 11.85, 12.11.). Its infrared spectrum showed ν_{max} 3350 (OH), 1640 (OH), and 1740 cm.$^{-1}$ ($COOCH_3$). Gas–liquid partition chromatography, using a column (1.8 m. × 3 mm.) packed with 3% S.E. 30 Silicone on Gas-chrom A at 200° with argon (24 p.s.i.) as the carrier gas, showed a single peak of retention time 5.28 min., $[\alpha]_D$ −0.18° (*c* 10.0, ethanol). The racemic ester is reported[12] to have m.p. 51–52°.

Methyl 9-D-Hydroxyoctadecanoate.—A solution of 15 mg. of 9-D-hydroxyoctadecanoic acid[5] in ether was left with diazomethane for 4 hr. at room temperature. Removal of solvent and chromatography of the residue on silicic acid gave a quantitative yield of methyl 9-D-hydroxyoctadecanoate, m.p. 51–52°. A mixture melting point with the sample (m.p. 50–51°) obtained from methyl helenynolate was undepressed, and the infrared spectra and O.R.D. curves of the two samples were identical. The compound showed a single peak with the same retention time (5.28 min.) on gas chromatography both when injected alone and when admixed with the hydrogenation product: $[\alpha]_D$ −0.18° (*c* 10.0, ethanol); O.R.D. (*c* 10.0, ethanol) $[\alpha]_{580}$ −0.20°, $[\alpha]_{240}$ −2.50°.

(−)-Methyl 12-D-hydroxyoctadecanoate had $[\alpha]_D$ −0.37° (*c* 12.2, $CHCl_3$); O.R.D. (*c* 9.0, ethanol) $[\alpha]_{580}$ −0.33°, $[\alpha]_{240}$ −2.31°.

(+)-Methyl 12-L-Hydroxyoctadecanoate.—Prepared from the preceding ester by an adaptation of the method of Schroepfer and Bloch,[10] this had $[\alpha]_D$ +0.36° (*c* 8.8, ethanol); O.R.D. (*c* 8.8, ethanol) $[\alpha]_{580}$ +0.38°, $[\alpha]_{240}$ +2.32°.

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[6] (a) K. Serck-Hanssen, *Chem. Ind.* (London), 1554 (1958); (b) K. Serck-Hanssen and E. Stenhagen, *Acta Chem. Scand.*, **9**, 866 (1955).

[7] F. D. Gunstone, *J. Chem. Soc.*, 1274 (1952).

[8] This compound has the *S* configuration on the convention of Cahn, Ingold, and Prelog.[9] It should be pointed out here that the use of the *R–S* convention makes natural (+)-methyl ricinoleate and the derived (−)-methyl 12-hydroxyoctadecanoate members of the *R* series owing to the operation of the sequence rule.

[9] (a) R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956); (b) R. S. Cahn, *J. Chem. Educ.*, **41**, 116 (1964).

[10] (a) G. J. Schroepfer, Jr., and K. Bloch, *J. Am. Chem. Soc.*, **85**, 3310 (1963); (b) G. J. Schroepfer, Jr., and K. Bloch, *J. Biol. Chem.*, **240**, 54 (1965).

[11] The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

[12] S. Bergström, *Arkiv Kemi, Mineral. Geol.*, **A21**, No. 15, 1 (1945).

Coumarins from 2-Hydroxyaryl Acids and Malonic Acid

L. L. WOODS[1] AND D. JOHNSON

Texas Southern University, Houston, Texas 77004

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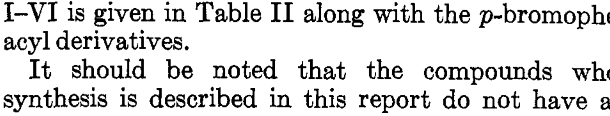
In previous papers it has been shown that coumarins can be prepared by the action of cyanoacetic acid on certain polyhydroxyaryl acids.[2] Subsequently, coumarins were prepared by the action of aldehydes on malonic acid in basic media.[3] In this contribution, a new method of preparing coumarins is presented in which 2-hydroxyaryl acids react with malonic acid in the presence of trifluoroacetic acid at carefully controlled temperatures to form 4-hydroxy-3-coumarincarboxylic acids—a rare subclass of coumarins.[4]

Since we have been unable to accomplish attack by an ester or acid on a phenol or monohydroxyphenol containing a powerful electrophilic group on the ring in the presence of trifluoroacetic acid, we have concluded that it is the carboxyl group of the aryl acid which has attacked the very active methylene group of the malonic acid which by the principle of vinylology is activated from two directions.

Attempts to decarboxylate compound I by the method of Adams and Bockstahler[5] failed, which is entirely understandable since a 4-hydroxycoumarin-3-carboxylic acid is the enolic form of a 3-carboxylic acid of a 2-pyronone which would not be decarboxylated by such mild reagents.

The equation for the reaction as visualized for compound I is expressed by eq. 1 and may be used as the model for the other members of the series. In Table I some of the properties of the compounds are given. A tabulation of spectral characteristics of compounds I–VI is given in Table II along with the *p*-bromophenacyl derivatives.



(1)

I

It should be noted that the compounds whose synthesis is described in this report do not have any pronounced fluorescence, do not show any absorption

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[1] The person to whom all communications regarding this contribution should be directed.

[2] L. L. Woods and J. Sterling, *Texas J. Sci.*, **15**, 200 (1963).

[3] L. L. Woods and J. Sapp, *J. Org. Chem.*, **30**, 312 (1965).

[4] M. Covello and E. Piscopo, *Gazz. chim. ital.*, 88 (1958).

[5] R. Adams and T. E. Bockstahler, *J. Am. Chem. Soc.*, **74**, 5346 (1952).