models of α-D-hexosides reveals extensive interference between the hydrogen atom of carbon 4 and the oxygen atom at carbon 1 in the 1B conformation, an interference not present in the proposed galactoside shift C1 ⇄ B2. It may be that the 1B conformation is prohibited for steric reasons in the α-D-hexose (and pentose) series, or its energy level is so much greater than that of the other forms that it cannot be overcome by the tendency of a charged axial hydroxyl group to move to the equatorial position. It is noted that methyl β-D-guloside might be expected to show an alkali-sensitive rotation due to the shift of a C1 ⇄ 1B equilibrium.

The hypothesis that hydroxyl groups which are axially oriented in neutral solution move to equatorial positions under conditions of high alkalinity requires further confirmation. Work to prove or disprove the concept is in progress. No attempt will be made at this time to interpret the alkali-sensitive behavior of the disaccharide sucrose, beyond observing that since the simple α-glucopyranosides (and trehalose) fail to show the same type of behavior, it would be logical to attribute the observed effect to changes in the fructofuranoside portion of the sucrose molecule.

Acknowledgment.—Some of the glycosides employed in this work were supplied by Drs. N. K. Richtmyer and H. S. Isbell.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

4-Allylveratrole from *Anemopsis californica*

BY W. J. HORTON AND E. G. PAUL

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The steam distillable oil from rhizomes of *Anemopsis californica* contains 4-allylveratrole which contributes the pungency to the odor of the oil. A second compound of unknown nature greatly masks the spice-like odor. A number of 4-alkylveratroles and their 5-sulfonamides were prepared in an effort to identify the sulfonamide (2-propyl-4,5-dimethoxybenzenesulfonamide) derived from the natural oil.

Anemopsis californica has a distinctive odor with a faint undertone of a spicy material. Both leaves and rootstock contain the odorant which resides in the steam distillable oil. Since the woody rhizome was the richer source, oil was obtained from this portion of the plant and submitted to fractional distillation using a small Vigreux column. A redistilled sample gave analytical data in excellent agreement with $C_{12}H_{16}O_2$. Catalytic hydrogenation indicated a single olefinic bond and oxidation produced veratric acid which was confirmed by the preparation of veratramide. The ultraviolet absorption also suggested the veratryl ring[1] with the olefinic bond in a non-conjugated position. Synthetic work was therefore designed so as to determine the nature of the butyl group in hydrogenated *Anemopsis* oil. A comparison of synthetic 4-butylveratroles (Table II) with the alkylveratrole derived from the oil was facilitated by the preparation of a crystalline sulfonamide from the hydrogenated oil. However, re-examination of the original analysis became necessary when none of the synthetic 4-butylveratroles nor isoamylveratrole gave a sulfonamide identical to the unknown sulfonamide (Table III). Furthermore the analytical values obtained from the unknown sulfonamide indicated a propyl group rather than a butyl group. Subsequent samples of the oil submitted to analysis pointed to contamination in the original oil by compounds of higher carbon content so as to make the excellent agreement with the formula $C_{12}H_{16}O_2$ fortuitous. The preparation of 4-propylveratrole (Table II) and its sulfonamide together with the ultraviolet spectra identify this part of the original oil as 4-allylveratrole.

The acyl-3,4-dimethoxyphenones were prepared by the excellent procedure of Gardner[2] and are collected in Table I. Clemmensen reduction gave the corresponding 4-alkylveratroles (Table II) whose sulfonamides are presented in Table III.

We are greatly indebted to Prof. Walter P. Cottom of our Department of Botany for discussions and to Mr. L. Woodbury at Dixie College, St. George, Utah, who so kindly provided the plant material.

Experimental[3]

The plant material collected in the vicinity of St. George, Utah, was divided into rhizomes and stems, the rhizomes were washed in water to remove adhering soil and thoroughly air-dried. They were then passed through a food chopper to produce material of the appearance of a brown sawdust. A 200-g. portion was steam distilled until 6 l. of distillate was obtained. The distillate was saturated with sodium chloride and extracted with ether. The residual oil on distillation of the dried ether extract weighed 17.4 g. (8.7%). This oil was divided into three fractions by distillation: (a) 6.22 g. of pale yellow, b.p. 137–141° (23 mm.); (b) 5.38 g. of yellow green, b.p. 141–146° (23 mm.); and (c) 2.44 g. of green, b.p. 147–155° (23 mm.). All fractions gave a brown color with tetranitromethane and a negative test with ferric chloride except (c) which was dubious. Fraction (a) gave a red complex with picric acid but a solid picrate could not be obtained.

In a similar manner from 500 g. of rhizomes the following fractions were collected by distillation at 23 mm. through a 25-cm. Vigreux column: 0.40 g., 90–106°; 16.16 g., 135–141.5°; "Fraction C" 8.09 g., 141–143°; 11.67 g., 144–151° (total yield 7.3%).

By distillation of fraction b above, a sample was obtained for analysis.

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[1] *Cf.* R. Adams, C. K. Cain and H. Wolff, THIS JOURNAL, **62**, 732 (1940), who give the absorption curves for 4-methyl- and 4-*n*-amylveratrole.

[2] P. D. Gardner, *ibid.*, **76**, 4550 (1954).

[3] Melting points on analytical samples are corrected. Microanalyses are by Dr. K. W. Zimmerman, University of Melbourne.

TABLE I

3,4-DIMETHOXYPHENYL ALKYL KETONES

Alkyl	Yield,[a] %	M.p. or b.p., °C.	Mm.		Analyses, Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Ethyl	97.9	54.5–60.5[b]						
n-Propyl	91	52–57[c]		$C_{12}H_{16}O_3$	69.20	69.64	7.75	7.74
i-Propyl	87.3	117–126	0.1–0.7[d]					
i-Butyl	91.6[e]	143–141.5	0.22–0.16[f]	$C_{13}H_{18}O_3$	70.24	70.49	8.16	8.20

[a] Prepared (ref. 2) using 0.403 mole of veratrole, polyphosphoric acid and the appropriate acid at 60° for 2.5 hr. [b] Softens at 47.5°; reported m.p. 58–59° by R. C. Fuson, R. Gaertner and D. H. Chadwick, *J. Org. Chem.*, **13**, 489 (1948). [c] The analytical sample from aqueous ethanol and from ligroin melted at 54.4–55.2°. The oxime from aqueous ethanol and from petroleum ether (30–80°) followed by sublimation at 0.1 mm. melted at 73.3–74.5°. *Anal.* Calcd. for $C_{12}H_{17}O_3N$: C, 64.55; H, 7.68. Found: C, 64.58; H, 7.52. [d] Reported as a colorless liquid b.p. 116–117° (0.2 mm). The semicarbazone melted at 146.5–148°; reported m.p. 149–150° by G. Norcross and H. T. Openshaw, *J. Chem. Soc.*, 1174 (1949). [e] Pale yellow oil; from 0.215 mole of veratrole. [f] The analytical sample boiled at 134.5° (0.37 mm.). The oxime was an oil. The semicarbazone formed colorless short thick prisms, m.p. 183.4–185.7°. *Anal.* Calcd. for $C_{14}H_{21}O_3N_3$: C, 60.19; H, 7.58. Found: C, 60.43; H, 7.43.

TABLE II

4-ALKYLVERATROLES

Alkyl	Yield[a] % (mole of ketone)	B.p. °C.	Mm.	$n^{25}D$	$d^{25}{}_4$	λ_{max}^{EtOH}	log ϵ		Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Propyl	84.4 (0.2)	137.5–138[b]	21	1.5150	1.006	280	3.52	$C_{11}H_{16}O_2$	73.30	73.58	8.95	9.12
						229	3.94					
n-Butyl	73 (0.0481)	149–152[c]	23	1.5121	0.9918	280	3.58	$C_{12}H_{18}O_2$	74.19	74.25	9.34	9.32
						228	4.00					
i-Butyl	81.3 (0.0481)	134–136[d]	16	1.50935	0.9848	280	3.51			74.46		9.33
						228	3.96					
i-Amyl	68.3 (0.10)	143–141.5[e]	0.22–0.16	1.50735	0.9795	280	3.54	$C_{13}H_{20}O_2$	74.96	75.09	9.68	9.63
						228	3.97					

[a] By Clemmensen reduction from the ketone (Table I). [b] The analytical sample boiled at 147.5° (34 mm.); reported b.p. 244–245° (763 mm.) by Wl. Ipatjew, *Ber.*, **46,** 3589 (1913). [c] The analytical sample boiled at 156–156.5° (28 mm.); reported b.p. 126–129° (7 mm.) by A. Ya. Berlin and S. M. Sherlin, *Zhur. Obshcheĭ Khim.*, **18**, 1386 (1948) (*C. A.*, **43**, 2185f (1949)). [d] The analytical sample boiled at 150–151° (31 mm.). [e] The analytical sample boiled at 168–169° (34 mm.).

TABLE III

2-ALKYL-4,5-DIMETHOXYBENZENESULFONAMIDES[a]

Alkyl	M.p., °C. (cor.)		Analyses, % Calcd. C	Calcd. H	Calcd. N	Calcd. S	Found C	Found H	Found N	Found S
n-Propyl[b]	169.6–170.8[c]	$C_{11}H_{17}O_4NS$	50.94	6.61	5.40	12.36	51.17	6.73	5.10	12.25
n-Propyl	166–170[d]									
n-Butyl	135–135.4[e]	$C_{12}H_{19}O_4NS$	52.72	7.01	5.13	11.73	52.79	6.89	4.68	11.62
i-Butyl	152.7–153.7						52.78	7.00	4.83	11.24
s-Butyl	120.2–122[f]						52.57	6.93	4.71	11.53
i-Amyl	164.6–166.8[g]	$C_{13}H_{21}O_4NS$	54.33	7.37	4.87	11.16	54.27	7.28	4.41	11.08

[a] Prepared according to R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., p. 246. [b] From the hydrogenation of *Anemopsis* oil. [c] Colorless groups of thin rods. [d] Uncorrected; mixed with the compound above, m.p. 166.5–170.5° (uncor.). [e] Softens sharply at 116°; colorless flat diamonds. [f] Colorless short thick rods from aqueous ethanol. [g] Colorless short rods.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39; O, 16.64. Found: C, 74.89; H, 8.34; O, 17.0.

The fraction b.p. 144–151° (23 mm.) was redistilled collecting a portion, b.p. 129–130° (14 mm.). From the latter a cut, b.p. 146.5° (29 mm.), was analyzed; $n^{25}D$ 1.52925, $d^{25}{}_4$ 1.028; $\lambda_{max}^{ethanol}$ 230 mμ (log ε 3.83), 280 mμ (log ε 3.39).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92; O, 17.95. Found: C, 74.66; H, 8.22; O, 17.4.

Catalytic Hydrogenation of "Fraction C."—A redistilled portion (7.55 g.) of the 8.09-g. middle cut above with 60 ml. of absolute ethanol and 300 mg. of platinum oxide was shaken with hydrogen at slightly above atmospheric pressure. After absorption of one mole of gas, the reaction stopped. The catalyst was removed by filtration, and the alcohol was distilled *in vacuo*. Distillation of the residue gave a middle cut, b.p. 164–164.5° (66 mm.), $n^{25}D$ 1.5131.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; O, 16.47. Found: C, 74.92; H, 9.31; O, 16.0.

The residual material boiled at 144–145° (29 mm.) and was later redistilled for analysis, b.p. 143–144° (29.5 mm.), $n^{25}D$ 1.5125, $d^{25}{}_4$ 0.9969, $\lambda_{max}^{ethanol}$ 278 mμ (log ε 3.62), 228 mμ (log ε 4.05).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; O, 17.75. Found: C, 74.64; H, 9.07; O, 16.6.

Oxidation with Permanganate.—The reaction of 3.84 g. of the original oil with powdered potassium permanganate in aqueous pyridine[4] gave 1.5 g. of acid, m.p. 172–178°. The neutral equivalent was 177; for veratric acid, 182. After sublimation (0.17 mm.) and crystallization from benzene, it melted at 171.5–179.5°. On mixing with veratric acid from authentic veratraldehyde (m.p. 176.5–180°), the melting point was 176–181.5°.

The amide prepared from the acid melted at 162.5–167° and mixed with authentic veratramide (m.p. 162–165°) melted at 161–164°.

2-(3,4-Dimethoxyphenyl)-2-butene.—Methylmagnesium iodide from 5.62 g. (0.231 mole) of magnesium in 150 ml. of ether was allowed to react with 15 g. (0.0774 mole) of 3,4-dimethoxypropiophenone dissolved in 70 ml. of

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(4) J. E. Bucher, THIS JOURNAL, **32**, 374 (1910).

benzene. After refluxing for 1 hr. the product was isolated by the usual procedure. Material with a cinnamon-like odor, b.p. 147–167° (20–18 mm.), was divided by redistillation into a colorless liquid with a flower-like odor (2.3 g.), b.p. 120–155° (23–22 mm.), and a greenish-yellow liquid of similar odor, b.p. 154.5–159° (20–19.5 mm.). A sample of the latter on redistillation was colorless, b.p. 163° (27 mm.), n^{25}_{D} 1.5507, d^{25}_{4} 1.040, $\lambda^{\text{ethanol}}_{\max}$ 254 mμ (log ε 4.10) and end absorption.[5]

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.64; H, 8.50.

2-*sec*-**Butyl-4,5-dimethoxybenzenesulfonamide.**—Catalytic hydrogenation of 1.0 g. of the above olefin with 500 mg. of 5% palladium-carbon in 50 ml. of ethanol consumed 148 ml. of gas; calculated volume 138 ml. After filtration of the catalyst and distillation of the solvent, the residual oil was converted to the sulfonamide (0.63 g.) as indicated in Table III.

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[5] The shift to shorter wave length when an olefinic bond is conjugated at the 4-position of the veratryl ring system confirms the report on 4-propenylveratole; A. Hillmer and P. Schorning, *Z. physik. Chem.*, **168A**, 81 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

2-Pyrones. XXVI. Alkylidene Methylglutaconic Acids and 3,6-Dialkyl-5-carboxy-5,6-dihydro-2-pyrones from Methyl β-Methylglutaconate and Ethyl Isodehydroacetate and their Isomerization and Decarboxylation

BY RICHARD H. WILEY AND H. G. ELLERT

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The condensation of aliphatic aldehydes with methyl β-methylglutaconate gives alkylidene glutaconic acids (III) and carboxy-δ-lactones (IV). Comparable yields are obtained using ethyl isodehydroacetate in place of the glutaconate. Short-chain and branched-chain aldehydes give diacids (III); longer chain and unbranched aldehydes give carboxylactones (IV). Decarboxylation of these products gives the dienonoic acids VI and δ-lactones V. The lactones can be hydrolyzed to the corresponding acids and the preferred route to the isoprenoid acid, 3,7-dimethyl-2,4-octadienoic acid, is *via* decarboxylation of the dipotassium salt to the lactone which is then hydrolyzed. The carboxy isoprenoid acid, γ-isoamylidene-β-methylglutaconic acid, has been obtained in three forms, m.p. 149–150, 163° and 181–184°. The isomer m.p. 149–150° has been assigned the 4-*cis*-2-*trans* structure; the isomer m.p. 181–184° has been assigned the 2-*trans*-4-*trans* structure on the basis of comparisons of their infrared spectra with those of *cis* and *trans* β-methylglutaconic acid. The δ-lactone structure has been established by conversion to the tetrahydro-2-pyrone structure with properties similar to those of other known tetrahydro-2-pyrones.

One of the few known methods for adding an isoprenoid unit to an organic structure involves the base-catalyzed condensation of dimethyl β-methylglutaconate (II) with an aldehyde[1-4] to give γ-arylidene or alkylidene-β-methylglutaconic acids (III). Although previously utilized principally for the synthesis of vitamin A, this method also makes possible the synthesis of acyclic isoprenoid acids of 10 or 15 carbons, which are of current interest as possible intermediates in the biosynthesis of cholesterol[5-8] with varying substituents, notably a 4-carboxyl group. Since previous studies of the reaction have not included comprehensive studies of the scope of the reaction using aliphatic aldehydes, we have undertaken a study of such reactions which we wish to record here along with our observations on the previously unreported accompanying cyclization to lactones (IV), the decarboxylation, and the geometrical isomerism of the γ-alkylidene-β-methylglutaconic acids (III). Particular attention has been directed to 3,7-dimethyl-2,4-octadienoic acid—an isomer of geranic acid and its 4-carboxy derivative.

The condensation reaction previously has been conducted using the aldehyde and dimethyl β-methylglutaconate (II) in methanolic potassium hydroxide. With aliphatic aldehydes the reaction is exothermic and the crystalline potassium salt of the product begins to precipitate shortly after mixing the reactants. The products from aliphatic aldehydes have been isolated in 51–91% yields (Table I). Since the β-methylglutaconate itself is formed readily from ethyl isodehydroacetate (I) by the action of methanolic potassium hydroxide, the utilization of the latter in place of the β-methylglutaconate to give the products directly in one step has been examined and found to be satisfactory. The products obtained by the two processes are comparable in all respects observed. This reaction is also exothermic and gives comparable yields with hexaldehyde (55 as compared to 58%), heptaldehyde (48 as compared to 51%), and pelargonaldehyde (61 as compared to 76%). With isobutyraldehyde (59 as compared to 91%) and isovaleraldehyde (43 as compared to 84%), the yield is noticeably poorer. Allowance for a 75% yield from isodehydroacetate to β-methylglutaconate indicates that the one-step process gives comparable yields with considerable saving of effort by avoiding isolation of the intermediate ester. The combined one-step process has been used with several other aliphatic and aromatic aldehydes listed in Table II. β-Ethoxypropionaldehyde, tiglic aldehyde and acetaldehyde failed to give characterizable products.

A unique feature of this reaction, which has not been recognized previously, is that not only diacids III but also the isomeric carboxylactones IV are

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[1] F. Feist and O. Beyer, *Ann.*, **346**, 117 (1906).

[2] C. D. Hurd and J. L. Abernethy, THIS JOURNAL, **63**, 976 (1941).

[3] V. Petrow and O. Stephenson, *J. Chem. Soc.*, 1310 (1950).

[4] J. D. Cawley, THIS JOURNAL, **77**, 4125 (1955).

[5] H. Rudney, *ibid.*, **76**, 2595 (1954); **77**, 1698 (1955).

[6] J. L. Rabinowitz and S. Gurin, *ibid.*, **77**, 1295 (1955); **76**, 3037, 5168 (1954).

[7] K. Bloch, L. C. Clark and I. Harary, *J. Biol. Chem.*, **211**, 687 (1954).

[8] S. Gurin, *et al.*, *Federation Proc.*, **14**, 752 ff. (1955).