ing the excess acetic anhydride was recrystallized from ethyl acetate–ligroin and formed colorless needles, m. p. 106–107.5°.

*Anal.* Calcd. for $C_{24}H_{22}O_{10}$: C, 61.27; H, 4.72; $—OCH_3$, 6.58. Found: C, 61.21; H, 5.00; $—OCH_3$, 6.45.

**Methylation of the Flavanone. The Methyl Ether, XII.**—Methylation of 0.30 g. of the flavanone (III), dissolved in methanol, with a fourfold excess of diazomethane in ether solution, afforded 0.195 g. of a compound as faintly yellow crystals, m. p. 139–140° after three recrystallizations from dilute alcohol.

*Anal.* Calcd. for $C_{19}H_{20}O_6$: C, 66.26; H, 5.86; $—OCH_3$, 36.00. Found: C, 66.27; H, 5.95; $—OCH_3$, 35.81.

**Oxidation of Leptosidin Trimethyl Ether. (A) With Hydrogen Peroxide.**—A solution of 0.50 g. of leptosidin trimethyl ether (VIII) in 50 ml. of acetone, 0.5 ml. of 50% aqueous potassium hydroxide and 7 ml. of 30% hydrogen peroxide was refluxed for two hours. After the addition of 2 ml. of saturated sodium bisulfite solution the acetone was removed under reduced pressure, 20 ml. of 1% hydrochloric acid was added and the solution was extracted with ether. The ether solution was extracted with three small portions of sodium bicarbonate solution and upon acidification of the bicarbonate extract a white precipitate formed (0.150 g.). This melted from 140° to 155° and repeated recrystallization did not raise or sharpen the melting point appreciably. The substance gave a purple color with ferric chloride. Its methoxyl content was intermediate between that of veratric acid and a dimethoxysalicylic acid.

*Anal.* Calcd. for $C_9H_{10}O_4$ (veratric acid): $—OCH_3$, 34.07. Calcd. for $C_9H_{10}O_5$: $—OCH_3$, 31.31. Found: $—OCH_3$, 32.62.

**(B) With Potassium Permanganate.**—Powdered potassium permanganate was added slowly to a hot solution of 0.60 g. of leptosidin trimethyl ether in 60 ml. of acetone until the purple color remained for five minutes. The solution was cooled and the solid collected by filtration. The solid was extracted with several small portions of hot water. Acidification of the aqueous solution so obtained yielded a white solid. A small additional amount was obtained by working up the acetone solution. After three recrystallizations from hot water the product (85 mg.) no longer gave a ferric chloride color and melted at 178–179.5°. An authentic sample of veratric acid melted at 179–180° and a mixture of this and the oxidation product melted at 178.5–179.5°.

*Anal.* Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.53. Found: C, 59.12; H, 5.69.

## Summary

1. From the ray flowers of *Coreopsis grandiflora* have been isolated luteolin (as the acetate) and three new substances: a glucoside, leptosin, its aglucon, leptosidin, and a flavanone.

2. Tentative structures have been assigned to leptosin, leptosidin and the flavanone, on the basis of (a) their compositions and those of their methyl ethers and acetates, (b) their distinctive color reactions and (c) biogenetic evidence from previous studies of flower pigments of related members of the *Compositae*.

LOS ANGELES, CALIFORNIA RECEIVED DECEMBER 23, 1942

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[CONTRIBUTION FROM THE CONVERSE LABORATORY, HARVARD UNIVERSITY]

# Normal Addition of Hydrogen Bromide to 3-Butenoic, 4-Pentenoic and 5-Hexenoic Acids in Hexane[1]

BY ARTHUR MICHAEL AND HOWARD S. MASON[2,3]

Evidence exists that non-polar solvents can induce abnormal addition of hydrogen bromide to terminally unsaturated aliphatic acids, but the independence of the character of this phenomenon has been controversial since the development of an understanding of the role of peroxides and oxygen in such reversals. The object of this investigation was to resolve this controversy[4,5] by determining whether or not the direction of addition of hydrogen bromide to such acids can be influenced by hexane under rigidly anti-oxidant conditions.

It has now been found that under these conditions 3-butenoic, 4-pentenoic, and 5-hexenoic acids in hexane solution add hydrogen bromide preponderantly normally (Table I).

(1) This paper was originally presented before the Organic Division at the Buffalo meeting of the American Chemical Society, September, 1942.

(2) Although this research was carried out under the direction of the late Professor Arthur Michael, the statements contained in this report, and the responsibility for them, are those of the junior author.

(3) Now at the National Institute of Health, Bethesda, Maryland.

(4) Gaubert, Linstead and Rydon, *J. Chem. Soc.*, 1974 (1937). "The persistent anomaly is the formation of the terminal bromo-acids in hexane or petroleum solution in the presence of hydrogen and anti-oxidant, which we have now observed in the case of five acids of the general formula $CH_2{=}CH[CH_2]_nCO_2H$ (where $n = 1$, 2, 3, 4, and 6) but which is not shown by undecenoic acid ($n = 8$), or by allylacetic acid in the experiments of Kharasch and McNab."

(5) Kharasch and McNab, *Chem. and Ind.*, **54**, 989 (1935). "The addition of hydrogen bromide to allyl acetic acid with . . . solvents [hexane] has now been repeated in this Laboratory . . . It is evident that these data are in complete agreement with our previous statements that peroxides and not the solvents control the direction of addition."

TABLE I

ADDITION OF HYDROGEN BROMIDE TO OLEFINIC ACIDS IN HEXANE SOLUTION

| Expt. | Moles[a] of acid | Solvent, cc. | Moles cat.[b] / Moles acid | Technique | Moles[d] of HBr | Time | Yield, % | Composition, % |
|---|---|---|---|---|---|---|---|---|
| | | | | 3-Butenoic acid | | | | |
| 1 | 0.008 | 1 | 0.0051 | Kharasch | 0.01 | 1 day | 100 | 100 $\beta$-Br[e] |
| 2 | .008 | 1 | .0051 | Kharasch | .01 | 1 day | 100 | 100 $\beta$-Br |
| 3 | .016 | 1 | .0051 | Kharasch | .02 | 1 day | 100 | 91 $\beta$-Br |
| 4 | .016 | 1 | .0051 | Kharasch | .02 | 14 days | 100 | 89 $\beta$-Br |
| 5 | .016 | 1 | .0051 | Kharasch | .02 | 14 days | 100 | 88 $\beta$-Br |
| | | | | 4-Pentenoic acid | | | | |
| 6 | .024 | 1 | .0059 | Kharasch | .03 | 1 day | 85 | 94 $\gamma$-Br[f] |
| 7 | .024 | 1 | .0059 | Kharasch | .03 | 10 days | 94 | 97 $\gamma$-Br |
| 8 | .024 | 1 | .0059 | Kharasch | .03 | 10 days | 96 | 96 $\gamma$-Br |
| 9 | .024 | 1 | .0059 | Kharasch | .03 | 12 days | 94 | 90 $\gamma$-Br |
| 10 | .024 | 1 | .0059 | Kharasch | .03 | 12 days | 95 | 89 $\gamma$-Br |
| 11 | .024 | 1 | .0059 | Linstead | .. | 1 day | 96 | 95 $\gamma$-Br |
| 12 | .024 | 1 | .0059 | Linstead | .. | 1 day | 98 | 97 $\gamma$-Br |
| | | | | 5-Hexenoic acid | | | | |
| 13 | .030 | 3 | .0069 | Kharasch | .06 | 2 days | 99 | 98 $\epsilon$-Br[f] |
| 14 | .030 | 3 | .001[c] | Michael | .06 | 1 day | 99 | 75 $\epsilon$-Br |
| 15 | .030 | 3 | none | Michael | .06 | 1 day | 99 | 94 $\epsilon$-Br |

[a] Accurate to 0.02 g. [b] Diphenylamine. [c] Benzoyl peroxide. [d] Accurate to about 0.1 g. [e] Correction applied (see original reference). [f] Accurate to ±1%.

## Experimental[6]

**Preparation of the Olefinic Acids and their Hydrobromides.**—3-Butenoic acid was synthesized from its nitrile. The nitrile was prepared according to the directions of Breckpot[7] and hydrolyzed to the acid by the method of Linstead.[8] The once-distilled product was refractionated in a high efficiency Fenske type column under a diminished pressure of nitrogen. The portion boiling at 81.5° at 23 mm. (manostat used), $n^{20}$D 1.4222, was used for the addition studies.

$\beta$-Bromobutyric acid was prepared by bubbling hydrogen bromide through molten crotonic acid until the theoretical weight increase was obtained. The product was allowed to stand in a vacuum desiccator over potassium hydroxide pellets for two days, and was then fractionated, boiling principally at 130° (25 mm.); crystallized from petroleum ether, the solid melted at 17°. Boorman, Linstead and Rydon[9] report 17–17.5°.

$\gamma$-Bromobutyric acid was prepared from 3-butenoic acid by hydrogen bromide addition to a solution of the olefinic acid in purified hexane in the presence of benzoyl peroxide. The reaction product was crystallized three times from petroleum ether, when it melted at 32–33°. The literature also reports a melting point of 32–33° for this compound.[9]

$\gamma$-Pentenoic acid and its hydrobromides were prepared by methods already described by Linstead, *et al.*[9,10]; only one variation was carried out, as noted below. The 4-pentenoic acid boiled at 67° (2 mm.), $n^{20}$D 1.4281; the earlier investigators reported b. p. 90° (16 mm.), $n$ 1.4283.[10]

The yield of $\gamma$-valerolactone, an intermediate in the synthesis of 4-bromopentanoic acid, prepared by Wohlgemuth's method,[11] was 46%. The following procedure was found to be an improvement: 35 g. (0.30 mole) of levulinic acid (Eastman Kodak technical grade) and 13 g. (0.33 mole) of sodium hydroxide were dissolved in 48 cc. of water and the volume reduced to 60 cc. by evaporation. To the resulting solution was added 1 g. of Raney nickel and the mixture subjected to hydrogenation at 2000 lb. pressure and 135°. The product was acidified with 40 cc. of concd. hydrochloric acid and extracted with ether. Twenty-two and a half grams of $\gamma$-valerolactone, b. p. 67° (2 mm.), was obtained: yield, 75%.

$\gamma$-Bromovaleric acid prepared from this lactone melted at 21° after three recrystallizations from petroleum ether. The literature[9] reports 21–22.5°. $\delta$-Bromovaleric acid melted at 39.5–40°, comparing favorably with the reported value of 39–40°.[9]

5-Hexenoic acid was prepared by a series of reactions previously employed by Linstead and Rydon[12]: 3-$n$-butenol-1 was synthesized from allyl bromide, trioxymethylene and magnesium; this was converted to its bromide with phosphorus tribromide in pyridine and the bromide malonated. The ester was then hydrolyzed and decarboxylated. It was found possible to increase the yield of the first step of this series from the original 42 to 72% by employing Gilman's directions for the preparation of allylmagnesium bromide[13] and Ziegler's method for the formaldehyde–Grignard reaction.[14] The final product, purified through its sodium salt in the usual manner and fractionated by vacuum distillation, boiled at 107° (17 mm.), $n^{20}$D 1.4343. These constants are identical with those of the purest previously prepared sample.[12]

$\delta$-Bromovaleric acid was also prepared by a synthesis already described[12]; it boiled at 114–115° (2 mm.). $\epsilon$-Bromocapric acid was prepared by the addition of

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(6) All melting points and boiling points reported were obtained by total immersion methods.

(7) Breckpot, *Bull. soc. chim. belg.*, **39**, 465 (1930).

(8) Linstead, Noble and Boorman, *J. Chem. Soc.*, 557 (1933).

(9) Boorman, Linstead and Rydon, *ibid.*, 568 (1933).

(10) Linstead and Rydon, *ibid.*, 580 (1933).

(11) Wohlgemuth, *Ann. chim.*, **2**, 298 (1914).

(12) Linstead and Rydon, *J. Chem. Soc.*, 1995 (1934).

(13) Gilman, *Bull. soc. chim.*, **43**, 1322 (1928).

(14) Ziegler and Tiemann, *Ber.*, **55**, 3406 (1922).

hydrogen bromide to 5-hexenoic acid in hexane solution in the presence of ascaridole. After removal of excess hydrogen bromide in a vacuum desiccator over potassium hydroxide pellets for two days, the product was purified, once by retaining the last third of a slow melt, and twice by recrystallization from low boiling petroleum ether. The product melted at 30–32° and contained 99.3% of the theoretical amount of bromine. Marvel and co-workers[15] report a m. p. of 35° for this compound.

**Preparation of Reagents and Techniques of Hydrogen Bromide Addition.**—The solvent "hexane" was prepared from a low boiling petroleum cut (Paragon Testing Laboratories "hexane," practical, b. p. 62–67°) by shaking with concentrated sulfuric acid until no diminution in volume occurred, then washing with alkali and distilled water, drying over sodium wire after shaking with anhydrous sodium sulfate, and distilling through a Vigreux column, the fraction boiling at 65–67° being taken and stored over sodium wire. Ascaridole, benzoyl peroxide and diphenylamine were Eastman Kodak Co. chemicals. Hydrogen bromide was prepared catalytically by the method of Ruhoff, Burnett, and Reid.[16] An all-glass system was employed, the generator being operated for about five minutes previous to use to sweep out traces of oxygen, and the hydrogen bromide being passed over a column of phosphorus pentoxide on glass wool and a column of bright copper mesh before admission to the reaction vessels.

Three techniques of addition of hydrogen bromide to the olefinic acids were used. The first was that employed by Linstead.[9] When diphenylamine was used as anti-oxidant a white solid precipitated as soon as the gas entered. This was, of course, the hydrobromide of the amine. The U-tubes were opened after twenty-four hours and the excess hydrogen bromide and the solvent removed by careful application of vacuum. The tubes were then placed in a vacuum desiccator over potassium hydroxide pellets at about 25 mm. and allowed to stand at 10° for twenty-four hours. The product was taken up in petroleum ether and the insoluble diphenylamine hydrobromide filtered off. The solvent was then again removed at low pressure and the bromo acids allowed to stand over potassium hydroxide and paraffin wax for a day. They were then analyzed for bromine content and for composition.

The technique regularly used in this Laboratory for hydrogen bromide addition studies utilized a Pyrex system involving a two-armed vessel, one side an 8-mm. condensing tube calibrated for weights of liquid hydrogen bromide at −72°, the other a 25 cc. round-bottomed flask. The apparatus was carefully steamed and flamed previous to use. The solution of olefinic acid in hexane was placed in the flask and protected from moisture by a phosphorus pentoxide–glass wool drying tube; after attaching the system to the generator by a ground-glass joint both arms were cooled in carbon dioxide snow–chloroform–carbon tetrachloride mixture. The correct amount of hydrogen bromide was then condensed in the measuring tube (transparent Dewar used), the system was sealed off and allowed to warm slowly. Before opening, it was again cooled to minimize the danger of explosion. The products were then worked up as described above.

The third technique used was an approach to that of Kharasch and Mayo.[17] Here, after condensation of hydrogen bromide, the system was immersed in liquid nitrogen, the generator side of the reaction vessel sealed off, and the apparatus evacuated with an oil pump suitably protected against corrosion. A pressure of 2 mm. was reached in this manner and presumably even last traces of oxygen removed.

**Determination of Composition of Mixtures of Hydrobromides.**—Each mixture of hydrobromides was first analyzed for total bromine. From this figure was calculated the % bromo acids present in the mixture. Analysis consisted of treatment with excess alkali, acidification, and Volhard silver nitrate titration.

A method for the determination of composition of mixtures of $\beta$- and $\gamma$-butyric acids has been described in the literature.[9] It was found impossible to approach its accuracy (5% low for $\beta$-butyric acid) by application of the method developed for the other pairs (*vide infra*); accordingly, it was applied in this investigation.

The difference in the rate of reaction of the hydrobromides of 4-pentenoic acid with acid alcoholic silver nitrate provided the basis for clean-cut determinations of the composition of mixtures of them. In this procedure exactly 0.100 g. of sample was weighed out from a tared micro dropper and dissolved in 5 cc. of 95% ethanol. Twenty cc. of nitric acid, 1 to 4, was then added to the solution, and finally 25 cc. of 0.100 *N* silver nitrate from a calibrated pipet, taking precaution to keep the pipet exactly on the vertical and timing the drainage to fifteen seconds on a stop watch. Timing of the reaction was begun at the moment the pipet started to drain. The mixture was immediately thermostated at 27°; at fourteen minutes and forty-five seconds 5 cc. of iron indicator was added and at exactly fiteen minutes the mixture was titrated with 0.100 *N* ammonium thiocyanate. The first 19 cc. was added very rapidly, the remainder slowly until the end-point was reached. The whole titration usually consumed about one minute; under these conditions it was found that $\delta$-bromovaleric acid lost 7.0% of its bromine while $\gamma$-bromovaleric acid lost 93%. A composition–% reaction curve fell on a straight line; the accuracy was within 1%.

Omission of the nitric acid did not affect the rate of reaction of $\gamma$-bromovaleric acid, but speeded that of its isomer to 30% reaction in the same period.

Exactly the same procedure proved effective for the determination of composition of mixtures of hydrobromides of 5-hexenoic acid. In this case the primary bromide reacted to the extent of 5.6%, the secondary to 99.5%.

## Summary

1. Quantitative methods for the determination of composition of mixtures of the 4-pentenoic and of the 5-hexenoic acid hydrobromides have been developed.

2. By applying rigorous anti-oxygen techniques this investigation has shown that no dis-

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[15] Marvel, *et al.*, THIS JOURNAL, **46**, 2838 (1924).

[16] Ruhoff, Burnett and Reid in "Organic Syntheses," Vol. XV, C. R. Noller, Ed.-in-chief, J. Wiley and Sons, Inc., New York, N. Y., 1935, p. 35.

[17] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

crete "hexane effect" upon the orientation of addition of hydrogen bromide obtains with 3-butenoic, 4-pentenoic or 5-hexenoic acid.

BETHESDA, MARYLAND RECEIVED NOVEMBER 25, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

# Studies of Sulfonates. VII. Conductances and Densities of Sodium Ethyl-, *n*-Butyl-, *n*-Octyl-, and *n*-Dodecylbenzene-*p*-sulfonate Solutions

BY R. G. PAQUETTE,[1] E. C. LINGAFELTER AND H. V. TARTAR

Previous work in this Laboratory has been devoted to various studies of straight-chain aliphatic sulfonates and discussions of their properties as colloidal electrolytes.[2,3] This paper presents the results of similar work on the sodium salts of the straight-chain alkylbenzenesulfonates, endeavoring to show the effect of the benzene nucleus on micelle formation and thereby to throw new light on the latter process. Compounds of this type have previously received little study, although commercial detergents containing them in impure mixtures have been marketed for some years. The pure *n*-octyl- and *n*-dodecylbenzene-*p*-sulfonates have not previously been described. Two shorter chain compounds ethylbenzene-*p*-sulfonate and butylbenzene-*p*-sulfonate have been included in this study.

## Experimental

**Sodium Ethylbenzene-*p*-sulfonate.**—Ethylbenzene, b. p. 134–136°, (Eastman Kodak Company) was sulfonated according to Sempotowski's[4] directions and isolated as the barium salt which crystallizes well from aqueous solution. In contrast to his claim that only the para isomer is formed, about 30% of the product was found in the mother liquor in a much more soluble form which could be quite completely separated from the para isomer. The para barium salt yielded well-formed, long, flat plates, probably orthorhombic, which were further purified by recrystallization; the other salt separated in clumps of very fine needles (compare with the butyl compound), and was evidently the *o*-ethylbenzenesulfonate.

The barium para-sulfonate, after purification by recrystallization, was converted to the sodium salt with a slight excess of sodium carbonate, and then purified by several crystallizations from alcohol in the form of colorless leaflets.

**Sodium *n*-Butylbenzene-*p*-sulfonate.**—*n*-Butylbenzene, b. p. 181–183°, (Eastman Kodak Company) was sulfonated. Balbiano[5] used fuming sulfuric acid but is vague in his directions. One hundred grams of butylbenzene was treated first with 7 cc. of concentrated sulfuric acid and then with 100 g. of fuming sulfuric acid. The sulfonic acid was isolated as the barium salt, which was difficult to separate from the barium sulfate.

Two isomers were found; the first, less soluble, in the form of small leaflets and in much greater quantity; the second, quite soluble and crystallizing in small spherulites; they have been designated as $\alpha$ and $\beta$, respectively, by Balbiano.[5]

The barium salt of the $\alpha$ isomer was purified by recrystallization from water and then converted to the sodium salt which was purified by recrystallization from alcohol, using purified animal charcoal to aid in removing impurities. The salt was finally obtained in small plates of rhombic outline; the yield was 23%.

The structure of the $\alpha$ salt was determined by the method outlined below.

**Caprylyl Chloride.**—To prepare the long-chain alkylbenzenes it was necessary to proceed by way of the alkylphenyl ketones, since direct alkylation results in isomerization of the alkyl chain. Caprylyl chloride was prepared in 82% yield by the method of Krafft and Koenig[6] from *n*-caprylic acid, m. p. 15–16°, (Eastman Kodak Company). The product, after two fractionations *in vacuo* through a 17-cm. Vigreux column, was colorless and boiled at 81.5–84.5° (cor., 15 mm.), the bulk coming over at 83°, in agreement with Krafft and Koenig. The melting point, taken on a large sample, was −63 to −62.5° (cor.). Deffet[7] gives the melting point as −61.0°.

***n*-Heptylphenyl Ketone.**—This compound was prepared from the caprylyl chloride and purified benzene by the Friedel–Crafts reaction. The yield was 91% of colorless product, nearly all boiling at 164–165.5° (cor., 15 mm.). Meyer and Scharvin[8] give the boiling point as 165° (15 mm.).

***n*-Octylbenzene.**—The above ketone (160 g.) was reduced at boiling temperature with amalgamated zinc foil squares and strong hydrochloric acid, the method of Clemmensen.[9] After twenty-two hours, 42 g. of crude octylbenzene was obtained. The residue was treated for

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[1] Standard Oil Company of California Fellow, 1939–41. Present address: U. S. Naval Academy, Annapolis, Md.

[2] Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

[3] Wright, Abbott, Sivertz and Tartar, THIS JOURNAL, **61**, 549 (1939).

[4] Sempotowski, *Ber.*, **22**, 2663 (1889).

[5] Balbiano, *Gazz. chim. ital.*, **7**, 345 (1877).

[6] Krafft and Koenig, *Ber.*, **23**, 2384 (1890).

[7] Deffet, *Bull. soc. chim. Belg.*, **40**, 385 (1931). In the original article the second digit of the number has failed to print well; the freezing point has consequently been misquoted by the abstract journals as −6.0. The second digit should be either a "4" or a "1," quite probably the latter. (Courtesy of M. L. Raney, Director of Libraries, University of Chicago.)

[8] Meyer and Scharvin, *Ber.*, **30**, 1943 (1897).

[9] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., **20**, 57 (1940).