

Source.....	Dunedin	Highcliffe	Kokonga	Momona	Ranfurly
I ₂ content, microgram/kg.....	18	62	21	74	58

As pointed out by the American workers, analyses of butter are of questionable value in the mapping of iodine-efficiency areas on account of the increasing use of iodized dairy feeds and salt licks.

Summary

The iodine content of butterfat may be determined by igniting a relatively small sample with caustic potash, extracting the iodide from the resulting potassium carbonate with alcohol and estimating the iodine by micro-titration using a standard thiosulfate solution.

DUNEDIN, OTAGO, NEW ZEALAND

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, NATIONAL TSINGHUA UNIVERSITY]

ALLYL LEVULINATE AND ITS DERIVATIVES¹

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RECEIVED JANUARY 11, 1932

PUBLISHED AUGUST 5, 1932

A number of alkyl levulinates² were recently synthesized and studied. Allyl levulinate, representing an unsaturated ester of levulinic acid, has not been reported in the literature. We have successfully prepared this new ester in a very pure condition by direct esterification of levulinic acid³ with allyl alcohol,⁴ using hydrogen chloride as the catalyst. Apparently at low temperature the extent of addition of hydrogen chloride on the ethylene linkage was too slight to affect the yield and the purity of the product. We have further allowed chlorine or bromine to add on the new ester and found the addition products to be identical in physical properties with those obtained by direct esterification of levulinic acid with β,γ -dichloropropyl or β,γ -dibromopropyl alcohol.

To characterize these three new esters, their corresponding semicarbazones and phenylhydrazones were prepared by the usual methods. They were carefully purified and their melting points determined. The experimental details are hereby communicated.

¹ This paper is from a thesis presented by Tsu-Sheng Ma to the Faculty of National Tsinghua University in partial fulfilment of the requirements for the degree of Bachelor of Science, July 1, 1931.

² (a) Sah and Ma. *THIS JOURNAL*, **52**, 4880 (1930); (b) Schuette and Cowley, *ibid.*, **53**, 3485 (1931).

³ (a) Schuette and Sah, *ibid.*, **48**, 1364 (1926); (b) Thomas and Schuette, *ibid.*, **53**, 2324 (1931).

⁴ Kamm and Marvel. "Organic Syntheses." John Wiley and Sons, Inc., New York, 1921, Vol. I, pp. 15-19.

Experimental

Preparation of Allyl Levulinate.—Into a cooled solution of 100 g. of levulinic acid in 200 cc. of allyl alcohol, 15 g. of dry hydrogen chloride was passed. After refluxing, the unesterified alcohol was distilled off on an oil-bath kept at 103°. The residue was fractionated under reduced pressure. The fraction boiling most constantly from 133 to 136° at 40 mm. was collected and purified by vacuum distillation; yield, about 60%.

Freshly distilled in a vacuum, allyl levulinate was a colorless liquid with a faint odor, insoluble in water, but soluble in all organic solvents. Distilled at atmospheric pressure, it boiled with decomposition at 219–222°. The simple physical constants of the pure product were determined and tabulated (see Table I).

Anal. Calcd. for $C_5H_{12}O_3$: C, 61.50; H, 7.75. Found: C, 62.05; H, 8.01.

Addition of Halogens on Allyl Levulinate.—Into a cooled solution of allyl levulinate in carbon tetrachloride, the calculated amount of dry chlorine or bromine was slowly introduced. The solvent was recovered. The residue was fractionated under a reduced pressure of 40 mm. The constant boiling fraction (β,γ -dichloropropyl levulinate at 199–202° and β,γ -dibromopropyl levulinate at 208–210°) was collected and purified by vacuum distillation; yield, about 40% of the theoretical.

Freshly distilled in a vacuum, they were colorless liquids with a faint disagreeable odor, insoluble in water, slightly soluble in carbon disulfide or carbon tetrachloride, but soluble in other organic solvents. Distilled at atmospheric pressure, considerable decomposition took place. The simple physical constants of the pure product were carefully determined and tabulated (see Table I).

To prove the identity of the addition products, β,γ -dichloropropyl⁵ and β,γ -dibromopropyl⁶ alcohols were prepared and directly esterified with levulinic acid. The esters thus obtained were found to be identical in physical properties to the corresponding addition products from allyl levulinate. For the sake of comparison, the simple physical constants of pure β,γ -dichloropropyl and β,γ -dibromopropyl alcohols were also determined and tabulated (see Table I). The halogen contents of the halogenated esters were determined by Stepanow's method⁷ (see Table II).

TABLE I
SIMPLE PHYSICAL CONSTANTS OF REAGENTS AND PRODUCTS

Name	B. p., °C.	d_4^{20}	n_D^{20}	Molecular refraction			
				Gladstone-Dale		Lorentz-Lorenz	
				Obs.	Calcd.	Obs.	Calcd.
β,γ -Dichloropropyl alcohol	183–185	1.3607	1.4819	45.67	45.70	27.02	27.33
β,γ -Dibromopropyl alcohol	214–215	2.0739	1.5466	57.49	56.28	33.30	33.18
Allyl levulinate	133–136 (40 mm.)	1.0277	1.4413	67.03	67.27	40.14	40.42
β,γ -Dichloropropyl levulinate	199–202 (40 mm.)	1.2357	1.4652	85.46	84.73	50.82	50.71
β,γ -Dibromopropyl levulinate	208–210 (40 mm.)	1.6580	1.5035	95.94	95.31	56.37	56.57

Semicarbazones.^{2a}—These were conveniently prepared by shaking the new esters with the calculated amount of semicarbazide hydrochloride and potassium acetate in alcohol solution. They were snow white crystals, insoluble in water. After being dried, their melting points were determined. The semicarbazone of allyl levulinate melted at 126–127°; that of β,γ -dichloropropyl levulinate, at 104–106°; while that of the dibromo analog melted at 101–102°. The nitrogen content of the first was determined by Dumas' method.

Anal. Calcd. for $C_9H_{15}O_3N_3$: N, 19.72. Found: N, 19.59.

⁵ King and Pyman, *J. Chem. Soc.*, 105, 1257 (1914).

⁶ Kohler, *Am. Chem. J.*, 42, 381 (1909).

⁷ Stepanow, *Ber.*, 39, 4056 (1906).

For the dihalogen derivatives, the halogen contents were determined by Stepanow's method (see Table II).

Phenylhydrazones.^{2a}—These were easily obtained by shaking the new esters with the calculated amount of phenylhydrazine in ethyl alcohol. The precipitation was instantaneous. The products, recrystallized from benzene and washed with ether, were snow-white crystals. The phenylhydrazone of allyl levulinate melted at 79–80°; that of the dichloro derivative, at 73–75°; and that of the dibromo analog, at 98–99°. The nitrogen content of the first was determined by Dumas' method.

Anal. Calcd. for $C_{14}H_{18}O_2N_2$: N, 11.39. Found: N, 11.6.

For the dihalogen derivatives, again Stepanow's method was used for the determination of their halogen contents (see Table II).

TABLE II
HALOGEN CONTENTS OF DERIVATIVES OF ALLYL LEVULINATE

Name	Formula	Subs., g.	AgNO ₃ used in cc. (0.1059 N)	Halogen, %	
				Found	Calcd.
β,γ -Dichloropropyl levulinate (I)	$C_8H_{12}O_3Cl_2$	0.2503	20.61	30.91	31.23
Phenylhydrazone of I	$C_{14}H_{18}O_2Cl_2N_2$.2533	15.01	22.24	22.36
Semicarbazone of II	$C_9H_{13}O_3Cl_2N_3$.2298	15.32	25.03	24.97
β,γ -Dibromopropyl levulinate (II)	$C_8H_{12}O_3Br_2$.2548	15.15	50.30	50.59
Phenylhydrazone of II	$C_{14}H_{18}O_2Br_2N_2$.2018	9.46	39.67	39.36
Semicarbazone of II	$C_9H_{13}O_3Br_2N_3$.3004	15.29	43.07	42.85

Summary

1. Allyl levulinate, a new ester, was prepared by the direct esterification of levulinic acid with allyl alcohol in the presence of hydrogen chloride.

2. Direct chlorination or bromination of allyl levulinate yielded β,γ -dichloropropyl or β,γ -dibromopropyl levulinates, identical with the products obtained by the direct esterification of levulinic acid with β,γ -dichloropropyl or β,γ -dibromopropyl alcohol.

3. The simple constants of β,γ -dichloropropyl alcohol, β,γ -dibromopropyl alcohol, and the three new esters of levulinic acid were determined.

4. The three new esters were characterized by their corresponding semicarbazones and phenylhydrazones.

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