After 3 recrystallizations, the product melted at 53.3–53.5° corr.

Subs., 0.2028: CO_2, 0.3026; H_2O, 0.0965.

Calc. for $C_5H_8O_5$: C, 40.52; H, 5.45.   Found: C, 40.69; H, 5.33.

The sample for the combustion had been weighed out in a boat inside a boat tube ("piggie") while the operation of running a blank determination and bringing the absorption train to constant weight was in progress. Just before commencing the combustion it was noticed that a small amount of the ester had sublimed to the top of the "piggie," and a new sample had to be taken.   This circumstance indicates the extreme volatility of this compound in the solid state.[1]

It is obvious that the reason for the lack of success in the attempt to prepare the substance by the dry hydrogen chloride method was the fact that the stream of gas removed the ester almost as fast as it was formed. The comparatively low and varying yields (about 50%) obtained by the method adopted may also be traced to the volatility of the dimethyl tartronate, since the distillate (*i. e.*, the solvent) always contained some ester of which only a small amount could be recovered.

NEW YORK, N. Y.

THE IDENTIFICATION OF ACIDS. VI. SEPARATION OF ACIDS BY MEANS OF PHENACYL ESTERS.

BY J. B. RATHER[2] AND E. EMMET REID.

In several recent papers[3] various crystalline derivatives of a number of organic acids have been described with the object of laying a foundation for the positive identification of such acids when found alone or in mixtures.   Having thus become acquainted with the derivatives prepared from individual acids, the first step towards unknown mixtures is a study of the separation of acids from unknown mixtures.   A number of such separations have been studied, special attention being given to mixtures likely to be met with in natural products.   This paper is a direct continuation of our work on phenacyl esters.[4]   The separations are given in detail so that one dealing with such mixtures may know just what to expect.

[1] Furthermore, it points out a possible source of error in conducting combustions of volatile solids—to eliminate which the sample should be weighed out immediately prior to the actual combustion.

[2] The experimental work described in this paper except that on phenacyl acetate was carried out in the laboratory of the Department of Agricultural Chemistry of the Arkansas Agricultural Experiment Station.

[3] THIS JOURNAL, **39**, 124, 304, 701, 1727 (1917); **41**, 75 (1919); **42**, 1043 (1920).

[4] *Ibid.*, **41**, 75 (1919).

Phenacyl bromide reacts with the sodium salt of a single organic acid, $C_6H_5COCH_2Br + NaO_2CR \longrightarrow C_6H_5COCH_2O_2CR + NaBr$, to form the phenacyl ester. When 2 such acids are present a mixture of the 2 phenacyl esters will be obtained and, if the solubilities of the 2 esters are sufficiently different, it may be expected that one or both of them may be obtained in pure enough form for identification, particularly with the aid of mixed melting points. Of 30 binary mixtures of acids, one constituent was identified in 28 cases, in 11 of which both were identified.

As noted in an earlier article, Hunaeus and Zincke prepared phenacyl acetate from the alcohol and acetanhydride and found the melting point to be 49°, while Hunnius obtained it from phenacyl bromide in alcohol solution, and observed a melting point of 40°. Our acetate prepared in dilute alcohol solution melted at 40°. We have prepared the same ester in glacial acetic acid solution both from phenacyl bromide and chloride and found a product melting at 49°. From sodium acetate and phenacyl chloride in water solution, the somewhat oily crude product melted at 40° but on long standing on absorbent paper, melted at 49°. No explanation is at hand for the discrepancy.

Method of Work.

The reagent and the method of work were essentially the same as previously used. Instead of 1.0 g. of the reagent in 15 cc. 63% alcohol, twice these quantities were employed. The acids, 0.005 mole of each, were dissolved in 10 cc. of water with enough sodium carbonate to convert them into the sodium salts, the mixtures being left slightly acid. The total salt present was equivalent to the 2.0 g. of reagent used, practically 0.01 mole, which was added with 20 cc. of 95% alcohol and the mixture boiled for 2 hours.

An unknown mixture of acids should be titrated with standard caustic soda and an amount of the resulting solution equivalent to 100 cc. of 0.1 N alkali, evaporated to small volume and made up to 10 cc. This solution should be slightly acid to avoid alcoholysis which is favored by the presence of free alkali.[1] It may be acidified by a trace of hydrochloric acid.

In the present experiments, the ester derived from 0.005 mole of an acid found itself in 30 cc. of the solvent instead of in 15 cc. as in the former work, and hence the amounts separating were somewhat different. The methods of manipulation were as nearly as possible the same as with the unmixed esters. The reaction mixture was cooled and filtered and the "first crop" obtained; the addition of several volumes of water gave the "second crop." In a few cases extra alcohol was added during the heating to keep the resulting esters in solution, and sometimes water had to be added to obtain a satisfactory "first crop." The weights and

[1] Lyman and Reid. This Journal. 42, 617 (1920).

melting points of the first and second crops were taken and the first crop recrystallized to constant melting point. From the way the first crop separates from the original reaction mixture, an estimate is made of the amount and strength of alcohol to be used in its recrystallization. In general it is boiled with 10 cc. of 95% alcohol under reflux, more being added if required to dissolve it. When all is dissolved water is added from a graduated pipet, until cloudiness results on slight cooling.

The recrystallization was thus carried on as in previous work, setting aside all the second crops of crystals, until one of the constituents was obtained in satisfactory purity, the melting point being then marked by an asterisk (*). The yields given are calculated on this fraction. A mixed m. p. was then made with the known ester. To identify the more soluble constituent the first "second crop," or several such second crops, was put through a similar series of recrystallizations. The crops so treated are designated by brackets ([ ]).

The results are given in tabular form, as in previous work, the first line representing the original preparation and succeeding lines the recrystallizations of the product. The melting points of the pure esters are given after the names of the acids.

In working with a mixture of unknown composition, it is advisable to prepare, for comparison and mixed melting points, the pure esters of acids suspected as being present.

Results.

Acids.	M. p. °C.	Solvent. Vol. Cc.	%	First crop. Wt. G.	M. p. °C.	Second crop. Wt. G.	M. p. °C.
Succinic	148	30	63	0.93	135–40	[0.32]	127–30
Tartaric	130	40	95	0.67	*148	0.12	122
*Mixed with succinate, m. p. 148°, identifying succinic; yield 75%.							
		15	63	0.19	*129	0.08	128
*Mixed with tartrate, m. p. 129°, identifying tartaric; yield 28%.							
Malic	106	30	63	0.42	90–5	[0.78]	105–10
Tartaric	130	15	63	0.23	*106	0.07	100
*Mixed with malate, m. p. 106°, identifying malic; yield 24%.							
		15	63	0.46	120	0.21	93–5
		15	63	0.20	123	0.20	106–10
		7.5	63	0.07	125–7	0.08	122
		5	47	0.04	*129	0.01	125
*This identifies the tartrate but with difficulty; yield 4%.							
Succinic	148	30	63	1.23	125–8	[0.12]	103–4
Malic	106	30	95	1.01	130–40	[0.16]	108–9
		35	95	0.70	144–6	[0.25]	106–7
		40	95	0.58	*148	0.04	123

*Mixed with succinate, m. p. 148°, identifying succinic; yield 65%. The presence of the malate increases the solubility of the succinic ester.

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
		Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		15	63	0.43	106–7	0.05	103–4
		5	95	0.35	106–7	0.06	106–5

*Characteristic curdy appearance of malate; yield 35%. The malate is difficult to identify.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Citric..........	104	30	63	0.75	....	[0.77]	85–90
		5	95	....	....	0.15	90–3
Malic..........	106	5	95	0.28	103–4	....	....
		5	95	0.25	*104	....	....

*Characteristic granular crystals, mixed with citrate, m. p. 104°, identifying citric; yield 35%. Mixed with malate, m. p. 90–2°, showing that it is not malate.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		15	63	0.28	90–2	[0.34]	88–90
		5	95	0.04	103–4	[0.19]	90.5
		5	95	0.07	100–1	[0.15]	95–9
		7.5	63	0.11	90–3	[0.18]	100–2
		7.5	63	....	....	0.14	*104

*Characteristic curdy and very bulky malate. Mixed with malate, m. p. 104–6; with citrate, m. p. 92–100°, showing that it is not malate; yield 5%. In this case the first crops were discarded as they had the appearance of the citrate and second crops recrystallized.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Succinic.........	148	30	63	0.95	....	[gum]	....
Citric..........	104	40	95	0.65	*148.5	0.17	95–8

*Mixed with succinate, m. p. 148.5°, readily identifying the succinic; yield 73%.

| | | 5 | 95 | 0.23 | *104 | gum | .... |

*Mixed with citrate, m. p. 104°, identifying the citric; yield 23%.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Citric..........	104	30	63	gum	....	[0.55]	....
		15	95	gum	....	0.44	95–100
Tartaric.........	130	5	95	0.14	*104.5	trace	....

Mixed with citrate, m. p. 105°, identifying citric; yield 14%.

| | | 15 | 95 | 0.16 | *129.5 | 0.29 | 95–100 |

*Mixed with tartrate, m. p. 130°, identifying tartrate; yield 17%.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Stearic..........	64	55	78	1.67	54–5	[0.21]	60–5
Palmitic.........	52.5	50	95	1.32	55–6	[0.13]	50–2
Half usual quan-		100	95	0.96	56–8	[0.12]	52.5
tities..........		50	95	0.70	61–2	[0.15]	53–4
		25	95	0.56	*64	[0.04]	52–4

*Mixed with stearate, m. p. 64°, identifying stearic; yield 56%.

| | | 25 | 76 | 0.35 | 53 | 0.05 | 50–2 |
| | | 25 | 76 | 0.26 | *52.8 | 0.03 | 52.8 |

*Mixed with palmitate, m. p. 52.5°, identifying palmitic; yield 33%.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Fumaric.........	197.5	30	63	0.35	180	[0.13]	148.5
Succinic.........	148	10^{a}	95	0.22	197	0.07	148.5

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
		Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		50[b]	95	0.05	*197.5	0	....

*The fumaric ester is readily identified since it is very slightly soluble in boiling 95% alcohol. In this preparation the larger part of the material was lost by bumping and spurting out.

[a] This was used to extract the succinate and the mixture was filtered hot.

[b] Only 0.05 g. was taken for recrystallization.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		5	95	0.10	*148.5	....	....

*This identifies the succinate.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Fumaric.........	197.5	30	63	0.70[a]	198	[0.37]	119
Maleic..........	119	60	95	0.05[b]	*198	0	....

*The fumaric is readily identified; yield 80%.

[a] Filtered hot.

[b] Only 0.05 g. taken for recrystallization.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		15	63	0.23	126	0.03	....
		15	63	0.14	*126	....	....

*This should be the maleic ester which, however, melts at 119°. A mixed m. p. was 126°. No reason for the divergence can be seen and the identification of the maleic acid is not considered satisfactory.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Benzoic.........	118.5	30	63	1.09	118.5	[0.49]	120
Tartaric.........	130	15	63	1.00	*118.5	0.04	118

*The benzoic is readily identified; yield 89%.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		20	95	0.20	130.5	0.20	125
		7.5	63	0.09	*130.5	0.07	130

*The tartaric is also readily identified; yield 9%.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Benzoic.........	118.5	30	63	1.35	113	[0.30]	90–3
Citric..........	104	30	95	0.53	181.8	0.75	105–10
		15	63	0.46	*118.8	0.05	117

*The benzoic is readily identified; yield 41%.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		5	95	0.20	100	0.03	115
		5	95	0.12	104	0.02	117
		5	95	0.08	*104	....	....

*The m. p. and the granular character identify the citrate; yield 8%.

Mixtures in which only one acid was identified.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Cinnamic......	140.5	50	76	1.58	115–20	0.63	100–8
Benzoic.........	118.5	40	95	0.86	140.5	0.66	108–10
		30	79	0.80	*140.5	0.04	140

*The cinnamic is readily identified, yield 57%. By repeated recrystallization of the second crops 0.45 g. was obtained melting at 112–3°, which gave a mixed m. p. of 113–6° with benzoate and a mixed m. p. 100–3° with cinnamate. This is evidently the benzoate but not pure enough for satisfactory identification.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Benzoic.........	118.5	30	63	1.95	95–9	0.16	90
Salicylic........	110	30	95	0.89	105–6	0.95	93

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
		Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
		15	95	0.52	110	0.33	98
		15	63	0.39	113	0.07	98
		15	63	....	113	....	105
		15	63	....	*115	....	106

*Mixed with benzoate, m. p. 118°, identifying it as benzoate but not quite pure. The salicylate could not be separated.

Acids.	M. p. °C.	Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Stearic..........	64	55	78	1.24	59–61	0.25	pasty
Oleic, oil........		25	95	0.76	64	0.10	pasty
Half quantities....		25	95	0.67	*64	0.02	63

*This identifies the stearic; yield 67%.

Palmitic..........	52.5	55	78	1.26	45–8	0.30	pasty
Oleic...........		25	95	0.50	52.8	0.30	pasty
Half quantities...		25	95	0.32	*52.5	0.12	52

*The palmitic is readily identified; yield 51%.

Stearic..........	64	50	76	0.84	64	oil	
Butyric, oil......		12	79	0.81	*64	trace	

*The stearic is readily identified; yield 81%.

Palmitic.........	52.5	50	76	0.85	53	oil	....
Butyric.........		12	79	0.81	*53	trace	....

*The palmitic is easily identified; yield 93%.

Succinic.........	148	30	63	0.54	149	oil	....
Acetic..........	40	35	95	0.49	*149	0.02	148.5

*The succinic is readily identified; yield 55%.

Citric..........	104	30	63	0.44	85–90	oil	....
Acetic..........	40	5	95	gum	....	0.08	104
		5	95	20	*104	trace	....

*The citric acid is readily identified; yield 20%.

Malic..........	106	50	38	0.65	75–80	0.05	95–100
Acetic..........	40	15	63	0.13	106	0.23	104
		30	33	0.09	*106	trace	....

*The malic is readily identified.

Tartaric.........	130	50	38	0.03	100	0.20	126–7
Acetic..........	40	10	47	0.14	*130	0.03	130

*The second crop was recrystallized instead of the first. The tartaric is readily identified.

Benzoic.........	118.5	30	63	1.03	118	0.10	98
Acetic..........	40	30	63	0.90	*118.8	0.05	118.5

*Identification easy, yield 80%. the acetate passed through the filter as an emulsion with the mother liquor and was recovered by extracting with ether but would not solidify.

Succinic.........	148.5	30	63	0.69	148.5	oil	....
Butyric, oil......		50	95	0.64	*149	0.03	148.5

*Identification is easy; yield 72%.

Tartaric.........	130	30	63	0.61	130.5	0.14	112–5
Oxalic..........		7.5	63	0.44	*130.9	0.09	130

*The tartaric is readily identified; yield 46%.

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
		Vol. Cc.	%.	Wt. G.	M. p. °C.	Wt. G.	M. p. °C.
Citric..........	104	40	47	gum	....	....	....
Oxalic..........		20	47	gum	....	....	....
		5	95	0.26	104.9	....	....
		5	95	0.22	*104.0	....	....

*The citric is readily identified; yield 22%.

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
Malic..........	106	30	63	1.13	85	trace	....
Oxalic..........		20	47	0.78	95	trace	....
		20	47	0.55	106	trace	....
		15	63	0.36	110	0.12	106
		15	63	0.22	110	0.11	106
		20	47	0.14	*110	0.05	109

*The ester separated as needles unlike the apparently amorphous ester previously obtained. In view of the 4° difference in melting point and the difference in appearance, an analysis of the 6th crystallization, 1st crop, was made resulting.
Calc. for diphenacyl malate: C, 64.86; H, 5.13. Found: C, 64.97; H, 4.87.

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
Succinic.........	148.5	30	63	0.73	149.5	oil	....
Oxalic..........		40	95	0.70	*149.5	trace	....

*Mixed with succinate, m. p. 149.5°; yield 79%.

Acids.	M. p. °C.	Solvent.		First crop.		Second crop.	
Benzoic.........	118.5	30	63	1.09	118.5	0.02	118
Oxalic..........		20	47	0.98	*118.5	0.06	118

*The benzoic is readily identified; yield 87%.

Tartaric and gallic acids could not be separated, neither could malic and gallic.

Summary.

The results obtained show that phenacyl bromide is a valuable reagent for the separation and identification of acids. Of 30 mixtures of esters examined, both of the esters were separated in pure state in 11 cases and one component in 17 other cases. Especially good results were obtained with polybasic aliphatic acids in mixtures such as occur in fruits and other natural products.

The following acids have been separated and identified in the presence of each of the acids named.

Citric Acid, in the presence of succinic, tartaric, malic, benzoic, oxalic, and acetic acids.

Succinic Acid, in the presence of tartaric, malic, citric, oxalic, and acetic acids.

Malic Acid, in the presence of tartaric, succinic, citric, oxalic, and acetic acids.

Tartaric Acid, in the presence of succinic, malic, citric, benzoic, oxalic, and acetic acids.

Stearic Acid, in the presence of palmitic, oleic, and butyric acids.

Palmitic Acid, in the presence of stearic, oleic, and butyric acids.

Benzoic Acid, in the presence of salicylic, acetic, tartaric, citric, oxalic, and succinic acids.

Fumaric Acid, in the presence of maleic and succinic acids.

Cinnamic Acid, in the presence of benzoic acid.

BALTIMORE, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

A SULFIDE ALCOHOL, OR BUTYL MERCAPTO-ETHYL ALCOHOL.[1]

BY T. C. WHITNER, JR., AND E. EMMET REID.
Received December 23, 1920.

In a recent article from this laboratory,[2] the acid, $CH_3CH_2CH_2CH_2$-SCH_2COOH, was studied with respect to the influence of the sulfur atom on the chemical and physical properties. In the present investigation, the corresponding alcohol, $CH_3CH_2CH_2CH_2SCH_2CH_2OH$, has been studied with the same object in view.

This alcohol is obtained readily by the action of ethylene chlorohydrine on the sodium salt of butyl mercaptan in water solution. It is a colorless oil boiling at 92–3° at 3 mm. In its physical properties and in its reactions, it resembles one of the higher alcohols, though some differences are found. Its odor suggests a higher alcohol and a sulfide, though the odor of its acetate is much more like that of an acetate of a higher alcohol. The chloride and bromide are readily prepared from the alcohol by the usual methods, but it shows very slight tendency to combine with phthalic anhydride. The sulfur atom appears to exercise somewhat the same influence on the mobility of the groups in the β-position as in the sulfide acid and in mustard gas, though the influence is less evident here. The acetate of this alcohol is stable, while the diacetate corresponding to mustard gas is very unstable.

From the bromide, $BuSCH_2CH_2Br$, the sulfide, $BuSCH_2CH_2SBu$, was readily obtained, but the corresponding sulfide ether, $BuSCH_2CH_2OEt$, could not be prepared by heating the bromide with sodium ethylate, vinyl-butyl sulfide, $BuSCH : CH_2$, was formed instead. This substance added hydrobromic acid readily to give the original bromide instead of the secondary bromide, $BuSCHBrCH_3$ which we desired.

The properties of the alcohol and its derivatives are brought together in the following table.

TABLE I.

Compound.	B. p.	$d_{0°}^{0}$	d_{25}^{25}.	n_D 20°.
$BuSCH_2CH_2OH$	92–3° at 3 mm.	0.9828	0.9693	1.4800
$BuSCH_2CH_2OCOCH_3$	84° at 4 mm.	1.0043	0.9875	1.4648
$BuSCH_2CH_2Cl$	68° at 6 mm.	1.0315	1.0101	1.4825
$BuSCH_2CH_2Br$	74° at 3 mm.	1.2308	1.2089	1.6740

[1] This and the following article are from the Doctor's dissertation of Thomas Cobb Whitner, Jr.

[2] Uyeda and Reid, THIS JOURNAL, **42,** 2385 (1920).