TABLE I

POTASSIUM 1-NITROALKYL-1-NITRONATES

$RC(NO_2)_2^-K^+$ R	Yield, %	Ultraviolet Spectrum λ_{max} (log ϵ)	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Potassium, % Calcd.	Potassium, % Found
$CH_2CH_2NO_2$ (I)[a]	33	373.5 (4.24)[b]	16.58	16.57	1.84	2.08	19.35	19.10	18.02	17.99
$CH_2CH_2COOCH_3$ (II)	77	379 (4.23)[c]	26.08	25.75	3.07	3.07	12.17	12.40	16.98	16.95
$CH_2CH_2COC_6H_5$ (III)	17	379 (4.21)[c]	50.40	50.46[d]	4.23	4.13[d]	11.76	11.52[d]	14.14	13.99
$CH_2CH_2COCH_3$ (IV)	40	379 (4.22)[c]	28.03	27.98	3.30	3.38	13.08	13.39	18.25	18.23
$CH_2CH_2CONH_2$ (V)	87	379 (4.21)[c]					19.50	19.68		
CH_3 (VI)	81	381.5 (4.23)[e]								

[a] Ref. (1). [b] Solvent, water. [c] Solvent, dilute potassium hydroxide. [d] Analyses for carbon, hydrogen, and nitrogen were on 4,4-dinitrobutyrophenone, m.p. 77.0–77.7°, obtained by acidification of an aqueous solution of the potassium salt and recrystallization of the precipitated product from methanol-water. The same product, m.p. 77–78° has been reported as a product of the Michael reaction of dinitromethane with acrylophenone.[4] [e] L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957) report 381 (4.21).

probably resulting from deformylation which took place more rapidly than reduction.

EXPERIMENTAL[5]

Methyl 4,4,4-trinitrobutyrate,[6] 5,5,5-trinitropentanone-2, and 4,4,4-trinitrobutyramide[1] were prepared by the reaction of nitroform with the appropriate conjugated olefins.

4,4,4-Trinitrobutyrophenone.[7] A solution of 24.2 g. of 4,4,4-trinitrobutyryl chloride in 200 ml. of dry benzene was stirred vigorously at 9° while 13.4 g. of anhydrous aluminum chloride was added portionwise. The mixture was refluxed for 1 hr., cooled to room temperature, and the aluminum halide complexes were destroyed by the careful addition of ice and 6*N* hydrochloric acid. The organic phase was separated, washed with 5% sodium bicarbonate and with water, dried over anhydrous magnesium sulfate, and the solvent removed *in vacuo*. Recrystallization of the residue from hexane gave 21.0 g. (79%) of tan needles, m.p. 78.8–79.3°. A further recrystallization from hexane (charcoal) gave 18.2 g. (64%) of white needles, m.p. 78.8–79.3°.

Anal. Calcd. for $C_{10}H_9N_3O_7$: C, 42.41; H, 3.20; N, 14.83. Found: C, 42.54, 42.74; H, 3.26, 3.14; N, 14.18, 14.42.

The same compound has been prepared by the Michael reaction of nitroform with acrylophenone and reported[4] to melt at 80–81°.

Typical reduction procedure. One hundredth mole of the trinitromethyl compound in 20 ml. of methanol was added to 0.022 mole of potassium iodide in 50 ml. of methanol and either refluxed for 1 hr. or stirred overnight at room temperature. The black mixture was concentrated and the precipitated yellow salt filtered, washed with ether and recrystallized from methanol-water. The yields recorded in Table I do not result from any attempt to arrive at optimal conditions.

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[5] *Caution:* The compounds herein described are explosive in nature. Appropriate precautions should be taken in their handling.

[6] K. Schimmelschmidt, *Hunter Report BIOS 1919; 22/IG*, July 3, 1946.

[7] We are indebted to Dr. Rip G. Rice who performed this synthesis.

Alkaline Cleavage of a Homolog of Ricinoleic Acid

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Cleavage of ricinoleic acid derivatives in the presence of strong alkali at above 240°, to give decanedioic acid and 2-octanol, is well known.[1,2] Related research has been carried out on other hydroxy and keto compounds, and mechanisms for the cleavage reaction have been proposed.[2,3]

The major fatty acid of *Lesquerella lasiocarpa* seed oil, named lesquerolic acid, has been characterized as (+)-14-hydroxy-*cis*-11-eicosenoic acid.[4] When lesquerolic acid (93% pure; *cf.* Table I) was heated at 270–300° with sodium hydroxide, the reaction yielded principally dodecanedioic acid (Table I) and 2-octanol $[\alpha]_D^{25}$ − 0.2°. Slight levorotation of the 2-octanol obtained by alkali cleavage of ricinoleic acid has also been reported.[2] These cleavage products confirm the structure reported for lesquerolic acid[4] and indicate a probable area of utility of the new acid for the preparation of chemical intermediates.

The two unknown alkali cleavage products detected by gas-liquid chromatography, Table I, were not identified, nor was the source of the tetradecanedioic acid elucidated. In addition to the gas-liquid chromatography evidence, the dodecanedioic acid was identified by melting point in admixture with authentic dodecanedioic acid.

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(1) R. Adams and C. S. Marvel, *Org. Syntheses*, Coll. Vol. I, 366 (1946).

(2) G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.*, **1947**, 753 and references therein.

(3) R. A. Dytham and B. C. L. Weedon, *Tetrahedron*, **8**, 246 (1960) and references therein.

(4) C. R. Smith, Jr., T. L. Wilson, T. K. Miwa, H. Zobel, R. L. Lohmar, and I. A. Wolff, *J. Org. Chem.*, **26**, 2903 (1961).

The neutral products were separated into ketonic- and alcoholic-containing fractions by sodium bisulfite adduction. The 2,4-dinitrophenylhydrazone of the ketonic fraction was shown to be identical with the 2,4-dinitrophenylhydrazone of authentic 2-octanone by mixed melting point determination. The alcoholic fraction was oxidized by chromium trioxide in aqueous acetic acid, and the product was shown to be 2-octanone by comparison of its 2,4-dinitrophenylhydrazone with the 2,4-dinitrophenylhydrazone of authentic 2-octanone by paper chromatography and by mixed melting point. The 2-octanone was accompanied by a compound of undetermined origin, with *Rf* similar to that of heptanal-2,4-dinitrophenylhydrazone. This product was not further characterized.

TABLE I

GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF METHYL ESTERS

Component	% Ester
LESQUEROLATE CONCENTRATE	
C$_{20}$ Saturated	1
C$_{20}$ Unsaturated	2
Lesquerolate	93
C$_{18}$ Hydroxymonoene	4
ALKALI CLEAVAGE PRODUCTS (steam-nonvolatile)	
Unknown	1
Decanedioate	1
Dodecanedioate	90
Unknown	2
Tetradecanedioate	6

The respective yields of products from lesquerolic acid are comparable to the yields obtained when carrying out a similar alkaline cleavage of ricinoleic acid.[1,2]

EXPERIMENTAL[5]

Except where noted, methyl esters for gas-liquid chromatography[6] were prepared with diazomethane.[7]

Preparation of sodium lesquerolate. Coarsely ground seeds of *Lesquerella lasiocarpa* (431.9 g.) were extracted overnight in a Soxhlet apparatus with petroleum ether (b.p. 33–57°). The bulk of the solvent was removed on a steam bath under a nitrogen atmosphere and the remainder *in vacuo* with a rotating evaporator, yielding 113.2 g. of oil.

The mixed methyl esters of *L. lasiocarpa* seed oil were prepared by refluxing the oil (113.2 g.) for 2 hr. under nitrogen with methanol (3200 ml.) containing 1% sulfuric acid. Esters were isolated by ether extraction in the usual manner; acidic material was removed by washing the ethereal solution with 5% potassium carbonate and then with water. The ether was removed *in vacuo* with a rotating evaporator, yielding an oil (111.5 g.). The resulting ester preparation (110.4 g.) was partially distilled in a spinning band column[8] (reflux ratio 2:1–3:1, 0.3–1.4 mm. pressure, maximum vapor temperature 179°), and a concentrate (54.5 g.) of methyl lesquerolate (93%, Table I) was obtained as a residue from the distillation pot. The yield of methyl lesquerolate represents an 89% recovery of the original content. Some of the methyl lesquerolate was distilled; however, the bulk of the distillate consisted of nonhydroxy methyl esters.[9] The methyl lesquerolate concentrate (54.5 g.) was refluxed for 2 hr. under nitrogen with *N* ethanolic potassium hydroxide (655 ml.), and the saponification mixture was extracted with ethyl ether to remove 2.3 g. of unsaponifiables. The alkaline liquor was acidified with 6*N* hydrochloric acid, and the resulting acids were taken up in ethyl ether. The free acids (maintained in a nitrogen atmosphere) were made slightly alkaline to indicator paper (about *p*H 8) with *N* ethanolic sodium hydroxide. The solvent was removed *in vacuo* with a rotating evaporator, yielding the sodium soaps (52.9 g.).

Alkaline cleavage of sodium lesquerolate. The reaction pot was a 250-ml., three-necked, round bottom flask. The flask openings were fitted with an inlet from a steam superheater, a thermometer, and an adapter connected to a condenser. The reaction pot was charged with sodium lesquerolate (15.0 g.), sodium hydroxide (6.0 g., about 250% excess), and water (1 ml.). The pot was heated externally until the contents reached 200°; then superheated steam was passed through during 5 hr. so that the temperature was maintained at 255–350° (mostly at 270–300°). Some foaming occurred during the reaction.

Characterization of the reaction residue. The residue was heated (80–90°) with water (400 ml.), then acidified with 6*N* hydrochloric acid to *p*H 6–7. The oils which separated were removed by filtration, then the hot solution was further acidified to about *p*H 2. The solution was cooled resulting in a white precipitate which settled, and the accompanying scum was removed by skimming. The crude dodecanedioic acid was collected on filter paper, then heated with ethanol (400 ml.) and activated carbon (0.4 g.). The mixture was filtered, the warm filtrate was concentrated (300 ml.), diluted with water (400 ml.), and then cooled to 7°. The resulting crystals were collected and dried for 1 hr. at 95° to yield a grayish solid (2.07 g.) melting at 116–125°. A second crop of crystals was obtained after evaporating some of the solvent; this crop, together with the skimming residues, was heated with ethanol (200 ml.) and activated carbon (0.5 g.), filtered, cooled to 7°, and yielded a soft yellowish solid (0.85 g.) melting at 75–118°. The two solid products were triturated separately with petroleum ether (b.p. 33–57°; 50 ml. and 20 ml., respectively), filtered, and washed with additional petroleum ether (3 × 20 ml.); the yields were 1.61 g., melting at 124–127°, and 0.57 g., melting at 115–122°, respectively. The two partially purified yields were combined and ground together, the combined product melted at 120–126° and had a neutral equivalent of 122.3 (Gas-liquid chromatography analysis see Table I). The yield, based on the gas-liquid chromatography analyses, is about 21%. Lit. for dodecanedioic acid, m.p. 129°,[10] neut. equiv., 115.1.

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(5) All melting points were determined with a Fisher-Johns block and are uncorrected. 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.

(6) T. K. Miwa, K. L. Mikolajczak, F. R. Earle, and I. A. Wolff, *Anal. Chem.*, **32**, 1739 (1960).

(7) F. Arndt, *Org. Syntheses*, Coll. Vol. II, 165 (1943).

(8) Nester-Faust Intermediate Laboratory Type: 8-mm. bore, 24-inch column.

(9) For total composition of mixed esters see: K. L. Mikolajczak, F. R. Earle, I. A. Wolff, and Q. Jones, *J. Am. Oil Chemists' Soc.*, *in press.*

(10) A. W. Ralston, *Fatty Acids and Their Derivatives*, Wiley, New York, 1948, p. 327.

When the partially purified product (0.350 g.) was recrystallized from benzene (7 ml.) and washed with pentane-hexane, it yielded a solid (0.185 g.) melting at 123–125°; melting point of an admixture with authentic dodecanedioic acid (m.p. 128–129°) was 123–127°. Gas-liquid chromatography showed 93% dodecanedioic acid.

Characterization of the volatile reaction product. The volatile cleavage product was isolated by saturating the condensate with sodium chloride then extracting with ether; the ether extract was worked up in the usual manner. The crude reddish yellow liquid (2.02 g.) was distilled, yielding a pale yellow liquid (0.94 g., b.p. 165–185°). The distillate was treated with saturated sodium bisulfite solution (15 ml.) and let stand for 6 hr. The resulting addition product was successively filtered, washed with ether, then decomposed with 2*N* hydrochloric acid. The liberated product was taken up in ether and worked up in the usual manner to yield a liquid (0.024 g.). This product (0.024 g.) in ethanol (3 ml.) was treated with 2,4-dinitrophenylhydrazine (0.045 g.) solution.[11] The resulting 2,4-dinitrophenylhydrazone (0.010 g.) melted at 53–57°; recrystallization from ethanol (0.5 ml.) yielded a solid (0.004 g.) melting at 54.5–56°; melting point of an admixture with the 2,4-dinitrophenylhydrazone of authentic 2-octanone (m.p. 57–58°) was 55.5–57°. The ethereal solution of the unchanged product was purged with water (4 × 25 ml.) and dried over sodium sulfate, the ether was evaporated under reduced pressure to yield a liquid (0.85 g.), $[\alpha]_D^{25} - 0.2°$ (*c* 1.92, ethanol), which did not form a 2,4-dinitrophenylhydrazone. Gas-liquid chromatography indicated about 90% 2-octanol. The yield, based on gas-liquid chromatography analyses, is about 15%, compared to 23–25% reported for a similar cleavage of ricinoleic acid.[1]

Chromium trioxide oxidation of the alcohol.[12] A solution of chromium trioxide (0.7 g. in 1 ml. of water and 12 ml. of acetic acid) was added dropwise to a stirred solution of the alcohol (0.035 g. in 5 ml. of acetic acid). The reaction temperature rose rapidly to 35°, and it was maintained at 30–39° for 3.5 hr. The solution was diluted with water (150 ml.) and saturated with sodium chloride; the oxidation product was taken up in ether. The ether phase was washed with dilute sodium hydroxide, then with water, and was dried over sodium sulfate. When the ether was removed under reduced pressure, the yield was 0.015 g. of product which, when treated with a slight excess of 2,4-dinitrophenylhydrazine solution, yielded a 2,4-dinitrophenylhydrazone (0.015 g.) melting at 38–50°.

A combination of recrystallizations from ethanol and chromatography on alumina (eluting with benzene) yielded a product melting at 51–55°; mixed melting point with the 2,4-dinitrophenylhydrazone of authentic 2-octanone (m.p. 57–58°) was 51.5–56°.

A second crop of 2,4-dinitrophenylhydrazone derivative (0.007 g.), which melted at 55–65°, was obtained from the initial filtrate residue by a similar recrystallization and chromatography procedure.

The two crops of 2,4-dinitrophenylhydrazone derivative were chromatographed on paper[13] simultaneously with the 2,4-dinitrophenylhydrazone of authentic 2-octanone. The observed R_f value was 0.89 for each major spot, however, a 2,4-dinitrophenylhydrazone derivative, not easily discernible, was resolved from each of the two crops of 2,4-dinitrophenylhydrazone derivative, R_f 0.66.

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[11] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., Wiley, 1956, p. 219.

[12] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[13] D. F. Meigh, *Nature*, **170**, 579 (1952).

β-Haloethyl Acetoacetates

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The preparation of β-chloroethyl acetoacetate is described in the literature.[1] The preparation of β-bromoethyl acetoacetate from diketene and β-bromoethanol has been reported.[2] The preparation of β-iodoethyl acetoacetate to our knowledge has not been reported.

The β-bromo derivative was prepared by ester interchange of β-bromoethanol with ethyl acetoacetate. The iodo ester was prepared by the reaction of sodium iodide with β-bromoethyl acetoacetate to yield β-iodoethyl acetoacetate. Unsuccessful attempts were made to prepare β-fluoroethyl acetoacetate by halogen replacement from both the β-bromo and β-iodo esters with organic soluble fluorides. The previously unreported copper(II)chelate of β-bromoethyl acetoacetate was readily prepared.

EXPERIMENTAL

β-Bromoethyl acetoacetate. Two hundred sixty grams (2.0 moles) of ethyl acetoacetate, 300 g. (2.4 moles) of β-bromoethanol, and 10 g. of litharge were mixed and heated at 100–160° with stirring until 116 ml. of distillate was collected. Gas chromatography showed that the distillate was largely ethanol, and treatment of the distillate with *p*-nitrobenzoyl chloride yielded ethyl *p*-nitrobenzoate.[3] The mixture in the still pot was cooled, diluted with ether, and filtered. The ether was removed from the filtrate by distillation and the residue distilled at 10 mm. to yield 197 g. (48%) of material, b.p. 124–127°, n_D^{25} 1.4728. The forecuts in the distillation were unchanged starting materials.

Anal. Calcd. for $C_6H_9O_3Br$: C, 34.4; H, 4.3. Found: C, 34.67; H, 4.69.

The product gave a positive test for bromine[3] and had an infrared spectrum consistent with the structure of β-bromo-

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[1] A. B. Baese (to Carbide and Carbon Chem. Corp.), U. S. Patent **2,167,168** (1939); E. R. H. Jones, F. A. Robinson, and M. N. Strachan, *J. Chem. Soc.*, 87 (1946); H. Brintzinger and J. Janecke, *Ber.*, **83**, 103 (1950).

[2] C. O. Parker, *J. Am. Chem. Soc.*, **78**, 4944 (1956).

[3] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., New York, 1957, p. 61, 212.