granular crystals of the caprolactone dimer described in **B** separated (identified by mixed melting point).

The residue still remaining (41%) solidified to a paste on standing, and was obtained as a light colored powder melting at 51 to 53° after several crystallizations from alcohol. It was similar to the polyester described in **A**, but it had a somewhat lower apparent molecular weight.

Anal. Calcd. for $HO-[-(CH_2)_5-CO-O-]_{16}-H$: C, 62.7; H, 8.8; mol. wt., 1842. Found: C, 63.56; H, 9.08; mol. wt. (in freezing benzene) 1980, 1660.

When treated with hydrazine hydrate it yielded the hydrazide already described.

From the above described reaction of sodium ethylate on bromocaproic acid no monomeric lactone was isolated. It is, however, not permissible to infer that no caprolactone was formed, since hydrochloric acid was present, and this, doubtless, would strongly catalyze the polymerization of any caprolactone that might have been formed.[11]

Summary

ϵ-Caprolactone has been prepared for the first time. It is the principal product of the self-esterification of the corresponding acid. A small amount of the cyclic dimeric ester (14-membered ring) is formed at the same time. Under the action of heat ϵ-caprolactone is converted to a polyester of high molecular weight. The process is not easily reversible. This behavior is compared with that already observed for other cyclic and polyesters.

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[CONTRIBUTION FROM THE MACKAY CHEMICAL LABORATORY OF THE UNIVERSITY OF NEVADA]

Essential Oil in Desert Plants. III.
Examination of the Oil of Artemisia Tridentata Typica

BY MAXWELL ADAMS AND FRANCIS S. OAKBERG

The scattered stunted shrubs which grow on the arid plains and mountains of the western United States are collectively called sagebrush. The name is more correctly applied to the family of plants classed as *Artemisia* of which more than 30 varieties are listed (Coulter and Nelson). Of this group of plants the oils from *Artemisia Cana*,[1] *Artemisia Frigida*, *Artemisia Leudoviciana*[2] and *Artemisia Caudata*, have been extracted and some of their physical and chemical properties observed.

Artemisia Tridentata Typica, often designated as black sage, is widely distributed, its habitat extending very generally over the United States west of the Missouri River. It grows as a densely branched shrub from a half meter in height on the upland barren soils, to three or four meters on alluvial fans. The aromatic nature of the shrub is very conspicuous. After a summer shower of rain the desert atmosphere is usually highly charged with the odor of the plant. The leaves when crushed have a very pungent characteristic odor and when steam distilled yield an oil, the physical constants of which have been determined.[3] The oil is best secured from the leaves of the brush which has been cut in the late autumn and allowed to dry thoroughly. The leaves and small twigs are collected after being threshed from the larger branches. The dry leaves yield almost 1% of a colorless oil which on standing turns light yellow. It has a very strong odor and a camphor-like taste. A 180-g. portion of this oil, after redistilling with steam and drying over anhydrous sodium sulfate, was placed in a 500-cc. round-bottomed distilling flask fitted with a Glinsky ball and bulb fractionating column. The distilling flask was set in an oil-bath and fractionated several times at ordinary pressure (650 mm.). The table shows the result of the sixth fractionation.

TABLE I

Number	Temp., °C.	Oil, g.	Density at 25°
I	130–165	37.9	0.8752
II	165–175	12.4	.9081
III	175–185	10.6	.9266
IV	185–198	28.7	.9474
V	198–201	21.3	.9712
Residues		72.0	

The combined residues from the above distillations, which were not volatile at 200°, were then distilled under diminished pressure using the above type of apparatus with a Bruhl receiver. The table gives the results.

TABLE II

Number	Temp., °C.	Pressure, mm.	Oil, g.	Density at 25°
I	95–105	14	25.0	0.9413
II	105–115	14	9.9	.9223
III	115–125	14	8.1	.9225
IV	125–135	13	3.0	.9093
V	135–150	13	5.3	.9221
Residues			20.7	

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(1) Theo. Whittelsey, "Otto Wallach's Festschrift," Göttingen, 1909, p. 668.

(2) Rabak, *Pharm. Rev.*, **24**, 324 (1906).

(3) Adams, THIS JOURNAL, **49**, 2895 (1927).

Fraction I, Table I, was subjected to further fractional distillation at 650 mm. pressure and an 8.5-g. sample of oil obtained which came over between 130 and 150°. It had a density of 0.863 at 25°, $(\alpha)_D$ −1.02° at 20° in a 50% alcoholic solution. It gave a distinct aldehyde test with Schiff's reagent and produced the characteristic irritation of the nose and eyes which is so apparent when the vapors escape into the room from the retort in which the plant is being steam distilled. In order to secure a larger portion of this fraction a fresh charge of sagebrush was placed in the steam distilling apparatus and the vapors which failed to collect in the receiver when passed through a water condenser were dried by passing through a column of calcium chloride and then led through a condenser surrounded by solid carbon dioxide. The liquid thus obtained was distilled by Gattermann's method. It had a constant boiling point of 61° at 650 mm. pressure. It gave the characteristic aldehyde test with Schiff's reagent and readily produced a mirror with an ammoniacal silver solution.

Preparation of the Semicarbazone.—A small sample of this low-boiling oil was dissolved in an equal volume of alcohol, treated with an equal weight of semicarbazide hydrochloride dissolved in a small amount of water, and when treated with sodium acetate produced at once, on stirring, an excellent yield of silvery white, plate-like crystals. These were recrystallized several times from hot alcohol and the semicarbazone thus formed had a constant melting point of 184°.

Preparation of 2,4-Dinitrophenylhydrazone.—One-half gram of 2,4-dinitrophenylhydrazine was refluxed with 25 cc. of ethyl alcohol and 0.5 g. of the oil was added. The mixture was heated to boiling, cooled slightly, 0.5 cc. of concentrated hydrochloric acid was added, and again boiled. On cooling, reddish-orange crystals separated. When these were recrystallized from alcohol they had a melting point of 186°.

The properties of the semicarbazone and 2,4-dinitrophenylhydrazone of this aldehyde and of the corresponding compounds of isobutyl aldehyde are somewhat similar. A sample of isobutyl 2,4-dinitrophenylhydrazone was prepared for comparison. The colors of the samples were different and when mixed, dissolved in alcohol and recrystallized, the mixture showed a distinct lowering of the melting point, thus proving that the oil is not isobutyl aldehyde.

We have named the new aldehyde "Artemisal" and have observed the following properties. It has a density of 0.81 at 25°; it is very volatile, is a powerful lachrymator; when in dilute form it has the characteristic odor of sagebrush and is doubtless the aromatic substance which is present in the plant and in all the various fractions of the oil. An attempt was made to determine its molecular weight by the freezing point method but it polymerized so rapidly that no constants could be determined. It is soluble in alcohol and ether but the solution soon becomes turbid. The solution in chloroform and ethyl acetate appears more stable but organic solvents catalyze polymerization and mineral acids and alkalies cause immediate polymerization. Even when the pure aldehyde is kept at zero it polymerizes, and when polymerized it forms a hard, faintly yellowish, transparent solid which begins to decompose without melting at 200°. It is slightly soluble in chloroform but is practically insoluble in the other ordinary organic reagents.

Fraction II, Table II, after several distillations over sodium which destroyed the pungent odor, gave a sample which came over at 151–152° (650 mm.), with a density of 0.8652 and a rotation of $[\alpha]_D$ 1.73° at 20°. This fraction was α-pinene, for when treated with amyl nitrite in glacial acetic acid, it readily gave on addition of hydrochloric acid a yield of pinene nitrosochloride which, when purified by precipitating from chloroform with methyl alcohol, melted at 102°.

Fraction III, Table I, which distilled between 175 and 185° (650 mm.) and had a density of 0.9081 and an optical rotation power of $[\alpha]_D$ −1.05° at 20° was treated with resorcinol; a white crystalline mass separated out which when washed and dried melted at 75–76°. This sample was treated with dilute sodium hydroxide solution and the oil recovered. This oil was purified from oxidation products by distilling over metallic sodium and the sample thus obtained boiled at 176° (650 mm.) and gave a resorcinol addition product which melted at 80°, greenish colored crystals with potassium iodide, and an addition product with phosphoric acid. These tests show the presence of cineol.

Fraction IV, Table I, which distilled at 198 to 201° and had a density of 0.9712 and an optical rotation of −7.51°, when further fractionated gave a white crystalline solid which collected in the condenser and separated from the distillate when cooled to zero. After this solid had been dissolved in alcohol and reprecipitated several times by careful dilution with water, the purified product melted at 175.5° and had an optical activity of $[\alpha]_D$ −12.11° at 20° in 50% alcohol solution which indicated that the substance is the comparatively rare *l*-camphor. When treated with hydroxylamine it formed an oxime which melted at 119°, and with semicarbazide hydrochloride it formed the camphor semicarbazone which melted at 234°. From the amount of the camphor fraction and the pure solid obtained, there appears to be approximately 40% camphor in the original oil, yet all attempts to prepare the oxime, or semicarbazone, from the original oil were unsuccessful. Whittelsey[1] reports that the oil from *Artemisia Tridentata* contains no camphor. Besides the method of distillation described above, the camphor may be obtained by destroying the other terpenes present by oxidation. Several methods have been used but the most satisfactory one of these consists of mixing the oil with an equal volume of alcohol and then adding concentrated nitric acid. After the mixture stands for a few minutes heat is generated, a vigorous reaction takes place, and when the mixture is cooled the solid camphor separates. Agitation with a dilute solution of alkaline potassium permanganate for several hours will also destroy the natural solvents present and allow the camphor to separate.

Fractions II and III, Table II, which were separated under diminished pressure, also yielded considerable quantities of cineol and camphor.

The high boiling fractions (both those obtained at ordinary pressure and those at diminished pressure) were light green in color and their properties indicated the presence of sesquiterpenes but when examined no individual terpene was identified.

Conclusion

The oil of *Artemisia Tridentata* contains a highly volatile aldehyde, hitherto undescribed, which gives the characteristic odor to the plant. The following is the composition of the oil: artemisal 5%, α-pinene 20%, cineol 7%, *l*-camphor 40%, unidentified sesquiterpenes 12%, resins 16%.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PURDUE UNIVERSITY]

Some Citrate Derivatives and their Properties

BY W. E. DONALDSON AND R. F. MCCLEARY WITH ED. F. DEGERING

Though considerable work has been done on citrate esters,[1] it seemed desirable to repeat some of this work with a view to improving some of the procedures. As a result, very pure trimethyl citrate has been made and from it by alcoholysis the mixed esters, propyl dimethyl, butyl dimethyl, and amyl dimethyl citrates have been prepared for the first time.

Experimental Procedures

Dehydration of Citric Acid.—Anhydrous citric acid was made by the use of purified benzene in a continuous water extractor.[2]

Preparation of Trimethyl Citrate.—192 g. (1 mole) of anhydrous citric acid was placed in a flask and treated with 288 g. (9 moles) of absolute methyl alcohol (99.5% redistilled over caustic, b. p. 65.0–66.5°). This was equipped with a reflux condenser and an inlet tube leading beneath the surface of the liquid. The flask was heated on a steam-bath as a slow current of hydrogen chloride gas was bubbled through the inlet tube for a period of two hours, then refluxed gently for six hours, and finally the product was allowed to cool and crystallize (sometimes there is a tendency toward supersaturation). The crystals were filtered off and dried in a vacuum desiccator over a mixture of calcium chloride and potassium hydroxide. After a recrystallization from water, 167 g. (73% yield) of a product melting at 75.0–76.5° were obtained. This product was subjected to distillation in a Vigreux column, and there was obtained 109 g. of a substance that boiled at 120–128° at about 0.5 mm. pressure. This represented an over-all yield of 48.4% for a product with a m. p. of 75.5–76.5°. In a preparation of trimethyl citrate from silver citrate and methyl iodide, and also in one distillation, a product was obtained with a m. p. 75.5°.

Preparation of Propyl, Butyl and Amyl Dimethyl Citrates.—To 23.4 g. (0.1 mole) of pure trimethyl citrate were added 13.6 cc. (0.15 mole) of *n*-butyl alcohol and 0.1 g. of *p*-toluenesulfonic acid.[3] This mixture was refluxed gently on a hot-plate for twenty-four hours. The product was then extracted four times with 50-cc. portions of hot water to remove most of the unreacted trimethyl citrate. This extraction left a residue of nearly pure butyl dimethyl citrate which corresponded to about an 86% yield. This product was subjected to fractional distillation at low pressure in a small Vigreux column, and a fraction collected which represented a 78% yield as calculated from the trimethyl citrate. The product was a water white viscous oil with a bitter taste and a very faint odor.

TABULATION OF ANALYTICAL DATA AND OF PHYSICAL CONSTANTS

Citrate	Carbon, % Calcd.	Carbon, % Found		Hydrogen, % Calcd.	Hydrogen, % Found		Saponification No. Calcd.	Saponification No. Found		n_D^{20}	d_4^{25}	B. p., °C.
Trimethyl	46.13	46.13	45.71	6.03	6.00	6.02	78.03	78.01	78.18			98 (0.2 mm.)
Propyl dimethyl	50.35	50.72	50.76	6.92	6.96	7.03	87.38	87.49	88.38	1.4470	1.1774	106 (.05 mm.)
Butyl dimethyl	52.14	52.14	52.02	7.30	7.25	7.14	92.05	91.94	92.05	1.4477	1.1303	111 (.08 mm.)
Amyl dimethyl	53.76	53.83	53.81	7.64	7.60	7.61	96.72	97.60	98.18	1.4484	1.1447	121 (.2 mm.)

The propyl and amyl esters were prepared by a similar procedure, though the following differences were observed: (1) propyl dimethyl citrate is much more soluble in water than the corresponding butyl derivative, hence it is best to use less water in extracting the unreacted trimethyl citrate. (2) The amyl dimethyl citrate is less thermostable than the corresponding propyl and butyl esters.

Summary

Three new compounds, propyl, butyl and amyl dimethyl citrates, have been prepared and their

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[1] A comprehensive bibliography is presented in "Some Citrate Derivatives and their Properties," a thesis submitted to the faculty of Purdue University by Walter Ellsworth Donaldson in partial fulfilment of the requirements for the degree of master of science and chemistry, June, 1933.

[2] The apparatus used was similar to that described in "Organic Syntheses." John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 68.

[3] A comparative study was made of the catalytic effect of *p*-toluenesulfonic acid, benzenesulfonic acid, phenol-*p*-sulfonic acid and α-naphthol-*p*-sulfonic acid on the rate of alcoholysis. *p*-Toluenesulfonic acid was found to be about twice as good as benzenesulfonic acid and about three times as good as phenol-*p*-sulfonic acid. α-Naphthol-*p*-sulfonic acid had no apparent effect.