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%.

RENO, NEV. RECEIVED OCTOBER 23, 1933

[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^{20}_D	d^{25}_4	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.

constants determined. These derivatives were obtained from the alcoholysis of trimethyl citrate in the presence of the corresponding alcohol and a catalyst (*p*-toluenesulfonic acid). Some new constants are given for trimethyl citrate.

LAFAYETTE, IND. RECEIVED OCTOBER 23, 1933

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The Hydration of Unsaturated Compounds. I. The Hydration Rate of Isobutene in Dilute Nitric Acid

BY HOWARD J. LUCAS AND W. FERDINAND EBERZ

Introduction

The hydration of isobutene has been observed by others. Butlerow[1] found that dilute nitric acid (10%?) or very dilute sulfuric acid brings about the change at the ordinary temperature and Miklaschewsky[2] found that a 5-10% solution of formic, acetic or oxalic acid brings about the hydration, not only of isobutene but also of some pentenes and hexenes. Michael and Brunel[3] obtained tertiary butyl alcohol as well as the iodide in the reaction between isobutene and aqueous hydriodic acid.

Experimental

In this investigation the rate of disappearance of isobutene has been measured at 25° in aqueous solutions containing variable amounts of nitric acid and of potassium nitrate.

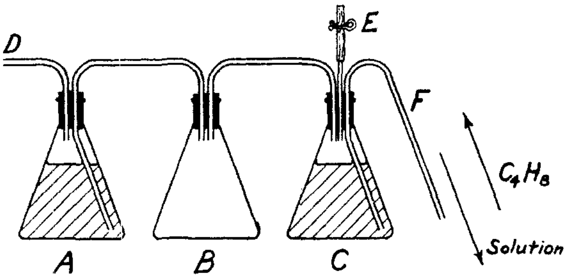

Fig. 1.—Apparatus for preparing aqueous butene solutions.

Materials.—The isobutene was prepared by refluxing tertiary butyl alcohol (Eastman's Pract.) with crystallized oxalic acid[4] and the evolved butene was passed through three spiral wash bottles each containing water in order to remove the alcohol, next through a tower containing soda lime and calcium chloride and then into a tube where it was condensed and sealed off until wanted. When needed the tube was opened and the evolved gas was passed directly into the water to be saturated.

Apparatus and Solutions.—The solution of butene in water of known acidity was prepared by passing butene through the flasks (500 ml.) shown in Fig. 1. The flask C contained a known volume of water at 25° and this was saturated, or nearly saturated, by passing in butene for one-half hour, shaking occasionally. The unabsorbed butene passed first into the empty flask B and then bubbled through the water in the flask A and finally through apparatus J (Fig. 2), filling it with butene. The butene solution was brought to the desired acidity by pipetting through E a known amount of standardized nitric acid. In those experiments in which the solution was brought to the desired ionic strength, a known amount of potassium nitrate was previously placed in the flask. After a thorough mixing the solution was forced, by blowing into the tube D, through F into the apparatus shown in Fig. 2. As the liquid was removed from C the butene in B took its place, so that there was always a butene atmosphere above the solution.

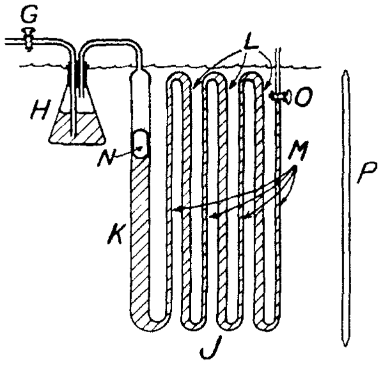

Fig. 2.—Apparatus in which the hydration of butene was carried out.

The liquid entered the apparatus J (capacity 240 ml., Fig. 2) at O, flowed down the four small vertical tubes M (30 cm. × 5 mm. bore) and up the three large vertical tubes L (30 cm. × 10 mm. bore) and finally filled the large vertical tube K (30 cm. × 20 mm. bore) in which the float N fitted snugly. About 150 ml. of solution was forced into the flask H (250-ml.) in order to wash out any liquid which had lost butene to the air. By this means H and J were filled with the solution to be examined. The apparatus was designed to allow withdrawals of samples of the solution without appreciable changes in composition. The float minimized the diffusion of butene into the air

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(1) Butlerow, *Ann.*, **180**, 245 (1876).

(2) Miklaschewsky, *Ber.*, **24**, ref. 26a (1891).

(3) Michael and Brunel, *Am. Chem. J.*, **48**, 267 (1912).

(4) Hurd and Spence, THIS JOURNAL, **51**, 2561 (1929).