92°); $[\alpha]^{20}D$ +68.6° (39 g. per 100 ml. of chloroform solution).

Anal. Calcd. for $C_{27}H_{21}O_6N$: N, 3.07. Found: N, 2.92.

Ethyl L-Norrhizocarpate (VII).—From Rhizocarpic Acid: A solution of 0.10 g. (0.0002 mole) of rhizocarpic acid and three drops of concentrated hydrochloric acid in 25 ml. of absolute ethanol was refluxed for twelve hours, then concentrated to 5 ml. Cooling produced 0.1 g. of the ethyl ester as minute yellow needles, 0.066 g. (64%) after two recrystallizations from ethanol, m. p. 170–170.5°. A mixed m. p. with rhizocarpic acid was 160–170°; with the ethyl ester described just below it was 169–171°.

From **Norrhizocarpic Acid.**—A solution was prepared from 0.2 g. (0.0005 mole) of the uncrystallized oily norrhizocarpic acid obtained from rhizocarpic acid, 1.0 ml. of concentrated hydrochloric acid and 50 ml. of absolute ethanol. This was refluxed for six hours, concentrated to 15 ml. and cooled to produce 0.12 g. (58%) of yellow needles, m. p. 169–170°. Recrystallization from ethanol raised the m. p. to 170–171°, $[\alpha]^{20}D$ 116.0 ± 2.2° (0.18 g. per 100 ml. of chloroform solution).

Anal. Calcd. for $C_{29}H_{25}O_6N$: C, 72.07; H, 5.17; N, 2.90. Found: C, 72.10; H, 5.19; N, 3.02.

L-Epanorin (II).—The same procedure as was employed for L-rhizocarpic acid, with 1.6 g. (0.012 mole) of L-leucine in place of L-phenylalanine, and the same quantities of the other materials, yielded 1.6 g. of crude L-epanorin, yellow needles which after one recrystallization from methanol weighed 0.91 g. (47%), m. p. 135–136°; $[\alpha]^{26}D$ −1.86 ±0.2° (6.48 g. per 100 ml. of chloroform solution). The levorotation was approximately one-half this value at 21°.

Anal. Calcd. for $C_{25}H_{25}O_6N$: C, 68.98; H, 5.74; N, 3.21. Found: C, 69.12; H. 5.71; N, 3.30.

A mixture of this compound with natural epanorin, m. p. 133.5–134.5°, melted at 133.5–134.5°.

The infrared absorption spectrum of L-epanorin in chloroform, unlike that of rhizocarpic acid, differed markedly from that of the crystalline solid (Fig. 1) in that the strong band at 1752 cm.$^{-1}$ of the solid was replaced by two medium bands at 1751 and 1772 cm.$^{-1}$.

DL-Rhizocarpic Acid (I).—The yield of amide, prepared in the same manner and with the same amounts of materials as was L-rhizocarpic acid, was 80%, yellow needles from ethanol, m. p. 144–145°.

Anal. Calcd. for $C_{28}H_{23}O_6N$: C, 71.66; H, 4.90; N, 2.99. Found: C, 71.77; H, 4.89; N, 3.01.

The infrared absorption spectrum of DL-rhizocarpic acid in chloroform solution was identical with that of the L-isomer. The spectrum of the crystalline solid differed from that of crystalline L-rhizocarpic acid in that the bands at 1740 and 1772 cm.$^{-1}$ of the L-isomer were replaced by a single band at 1754 cm.$^{-1}$ in the case of the racemic form.

Ethyl DL-Norrhizocarpate (VII).—This was synthesized in the same manner as was L-rhizocarpic acid, and with the same amounts of materials, except that the amino ester prepared was the ethyl ester of DL-phenylalanine instead of the methyl ester of L-phenylalanine. The yield was 72%, yellow needles from absolute ethanol, m. p. 143–144° (a mixed m. p. with the corresponding methyl ester, m. p. 144–145°, was 131–134°).

Anal. Calcd. for $C_{29}H_{25}O_6N$: C, 72.07; H, 5.17. Found: C, 72.26; H, 5.24.

DL-Epanorin (II).—The procedure analogous to that for L-rhizocarpic acid gave a 41% yield of DL-epanorin, yellow needles from methanol, m. p. 162–163°.

Anal. Calcd. for $C_{25}H_{25}O_6N$: C, 68.98; H, 5.74. Found: C, 68.89; H, 5.54.

The infrared absorption spectrum of DL-epanorin in chloroform was identical with that of the optically active material.

Pulvinic Acid Lactone (III) from Compounds I, II, VI and VII.—A solution of 0.1 g. (0.0002 mole) of L-rhizocarpic acid in 10 ml. of acetic anhydride was refluxed for two hours, then poured into 10 ml. of water and stirred until all the acetic anhydride had decomposed. Cooling to 5° resulted in the formation of yellow crystalline pulvinic acid lactone, 0.05 g. (74%), m. p. 219–221° (lit.,[12] 220–221°) after washing with cold water and one recrystallization from chloroform. This procedure with DL-rhizocarpic acid, ethyl L-norrhizocarpate and L-epanorin gave the same product in comparable yield. L-Norrhizocarpic acid gave the lactone, but in less than 20% yield.

Infrared Absorption Spectra.—The spectra were kindly furnished by Miss Elizabeth M. Petersen, using a Perkin–Elmer Model 12B infrared spectrometer with rock salt optics. The spectra of Fig. 1 were obtained with the crystalline pigments as Nujol mulls.

Summary

Rhizocarpic acid and epanorin, the only lichen pigments known to contain nitrogen, have been shown by synthesis to be the methyl esters of the pulvinic acid amides of L-phenylalanine and L-leucine, respectively. The synthetic materials are identical with samples of the natural pigments.

URBANA, ILLINOIS RECEIVED FEBRUARY 2, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF TORONTO]

Tripotassium 1,3,5-Triazacyclohexane-1,3,5-trisulfonate

BY W. P. BINNIE, H. L. COHEN AND GEORGE F WRIGHT

One of the processes developed in Germany for manufacture of Cyclonite (1,3,5-trinitro-1,3,5-triazacyclohexane, RDX) at the beginning of the second world war supposedly involved the preparation of potassium methylenesulfamate and its conversion to the explosive in 80% yield with nitric acid and sulfur trioxide.[1,2] The following reactions have been suggested as representative of this process

(1) $CH_2O + H_2NSO_3K \longrightarrow CH_2{=}NSO_3K + H_2O$

(2) $CH_2{=}N{-}SO_3K + HNO_3 \xrightarrow{SO_3} CH_2{=}NNO_2 + KNSO_4$

(3) $3CH_2{=}NNO_2 \longrightarrow (CH_2{=}N{-}NO_2)_3$

Reaction 3 of this series involves the trimerization of the hypothetical methylenenitrimine to Cyclonite. The propriety of this step seems questionable in view of earlier studies[3,4] which indicate that this monomer, if formed, decomposes at once to formaldehyde and nitrous oxide. No

(1) W. D. Crater, *Ind. Eng. Chem.*, **40**, 1627 (1948).

(2) See also P. B. reports 925, 1820 and 80,891 (1945).

(3) W. J. Chute, *et al.*, *Can. J. Res.*, **27B**, 218 (1949).

(4) E. Aristoff, *et al.*, *ibid.*, **27B** 520 (1949).

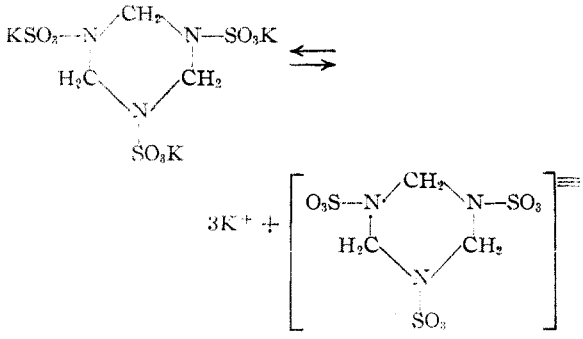
evidence has been found to indicate that it can polymerize. Accordingly it seemed advisable to examine this reaction series experimentally.

The potassium salt is obtained in yield about 50% of theoretical when ice-cold aqueous solutions of formaldehyde and potassium sulfamate are mixed and neutralized with aqueous potassium hydroxide to *p*H 5. This yield could be improved markedly by re-use of the mother liquors.

The salt does not have a satisfactory melting point, but it has been characterized by its X-ray powder diagram. It is insoluble in non-aqueous solvents and is largely recovered unchanged after attempts with thionyl chloride and sulfuryl chloride to convert it to the corresponding sulfonyl chloride. Titration with aqueous mineral acid shows that methylenesulfamic is comparable in strength with hydrochloric acid, but it is unstable. Nothing can be recovered after attempts to nitrosate with nitrous acid or to methylate with methyl sulfate. No success has attended attempts to reduce catalytically an aqueous solution of the potassium salt with platinum and hydrogen.

Goniometric studies with visible light and with X-rays (Cu K_α, using rotation, oscillation and moving film techniques) classify the salt as monoclinic prismatic. The unit cell includes atoms to a total weight of 3533. Extinctions are consistent with the space-group $C^5_{2L}(P2_{1/N})$ in which the general equivalent points are four-fold. The asymmetric unit thus comprises atoms of a weight total of 883. Since this weight is six times that of monomeric potassium methylenesulfamate these data from single crystal studies are not inconsistent with the possibility of a molecular weight three times that of the monomer. No contradiction resulted from Patterson and Fourier summations of calculated structure factors, available in our files.

It thus seems possible that potassium methylenesulfamate is trimeric. Further evidence for its trimeric nature has been provided by a cryoscopic molecular weight determination in water. Freezing point depressions have been determined for various concentrations as shown in Fig. 1 and extrapolated to infinite dilution. Calculation of the apparent molecular weights thus gives an extrapolated value of 114. Since the neutrality of the salt indicates that it would be completely dissociated at infinite dilution, this value of 114 approximates more closely to 111, expected for completely ionized trimer than to 74 which would represent the completely ionized monomer. Further evidence against the monomeric structure can be seen in Fig. 1 since the apparent molecular weight at high concentrations exceeds 148 which is maximum for the un-ionized monomer. These results are best explained by the following equilibrium.



It has been shown previously[5] that, while Cyclonite prepared from hexamethylenetetramine always is contaminated with 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane (HMX), this impurity is absent when the starting material contains a single preformed 1,3,5-triazacyclohexane ring. If, then, the condensation product of formaldehyde and potassium sulfamate were actually trimeric, and comprised such a ring system, the Cyclonite produced from it ought to show by its high melting point (204–205°) that it contained none of the tetramer, HMX. This was found to be the case when the crude product obtained from treatment of the salt with nitric acid and sulfur trioxide was purified by crystallization from nitric acid under conditions where the tetramer, HMX, would not have escaped detection if it had been present.

Incident to this preparation it was found that the sulfur trioxide could be replaced conveniently by phosphorus pentoxide in order to avoid the difficulties involved in manipulation of the sulfuric anhydride.

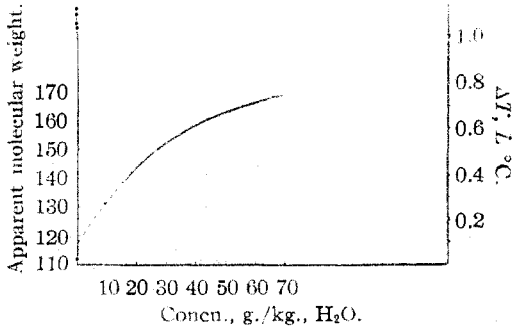


Fig. 1.

Experimental[6]

Tripotassium 1,3,5-Triazacyclohexane-1,3,5-trisulfonate.—A solution of potassium sulfamate, prepared in the cold from sulfamic acid and aqueous alkali, was filtered, chilled to 0° and treated with 75 ml. (1 mole) of 37% aqueous formaldehyde solution. The temperature rose to 20°, was recooled and neutralized to *p*H 5 with 20–30 ml. of 35% aqueous potassium hydroxide. The precipitate (64.5 g.) thus formed was filtered off from the chilled slurry. A second identical crop (8.5 g.) was obtained by slight dilution of the filtrate. This air-dried material thus represents 50% of the theoretical yield.

(5) Brockman, *et al.*, *Can. J. Res.*, **27B**, 469 (1949).

(6) All recorded melting points have been corrected against reliable standards.

Anal. Calcd. for CH_2NSO_5K: K, 26.5; CH_2O, 20.4. Found: K, 26.2; CH_2O, 20.0.

Monoclinic prismatic crystals for goniometric study are best obtained from water–ethanol solution. Rapid cooling produces needles, but thin plates, approximately hexagonal in cross section and developed on the 100 face are obtained by slow cooling. The cleavage of this plate (shown in Fig. 2) is principally parallel to the (001) and (011) faces. Its refractive indices are: α, 1.50 (parallel to the *b* axis); β, 1.505; γ, 1.515. Density by flotation was found to be 2.127 at 25°.

Unit cell dimensions (Å.) are $a = 14.32 \pm 0.04$, $b = 9.73 \pm 0.03$, $c = 20.11 \pm 0.06$ with $\beta = 102.3 \pm 0.3°$; the cell volume is thus 2737 cu. Å., which accommodates the atomic weight equivalent of 24 molecules of potassium methylenesulfamate. The axial lengths have been checked by the face-diagonal measurements, 001 = 22.30 Å. and 110 = 17.35 Å. Extinctions are consistent with space-group $C^5_{2h}(P_{2_1/n})$, namely, (*h*0*l*) when $h + l$ are odd and (0*k*0) when *k* is odd.

Spacings and relative intensities from the powder diffraction pattern serve in absence of satisfactory melting point as identification of the salt.

I/I_1	d/n	I/I_1	d/n	I/I_1	d/n	I/I_1	d/n
1.0	3.98	0.4	3.18	0.35	2.00	0.25	3.64
0.9	3.35	.4	3.10	.3	7.05	.25	2.11
.8	3.47	.35	8.71	.3	2.59	.2	6.39
.5	5.27					.2	2.46

The apparent molecular weight of the salt was determined by the freezing-point lowering of aqueous solution at several concentrations as shown in Fig. 1. The *p*H of these aqueous solutions was exactly 7.0.

1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)

A. From Phosphorus Pentoxide.—Into a 200 ml. three-necked flask equipped with a wide sweep powerful stirrer was placed 34.4 ml. (0.8 mole) of absolute nitric acid. The stirred acid, maintained at 0° was treated with 28.4 g. (0.2 mole) of phosphorus pentoxide over two minutes. This mixture was chilled and stirred while 29.4 g. (0.066 mole) of tripotassium 1,3,5-triazacyclohexane-1,3,5-trisulfonate was added over thirty five minutes so as to maintain a reaction temperature of 25–30°. After one hundred

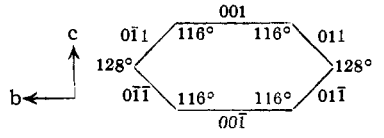


Fig. 2.

fifty minutes more at this temperature the whole was raked into ice (reverse dilution causes decomposition), filtered and washed with dilute ammonia. The vacuum-dried RDX (m. p. 195–197°) weighed 12.4 g. or 84% of theoretical. This was heated cautiously with 50 ml. of 60% nitric acid until by-product decomposition was complete after two minutes, then diluted with 50 ml. of water, cooled and filtered. The product, washed with 3% ammonia and vacuum dried weighed 11.8 g. and melted at 204.3–204.7°.

(b) From Sulfur Trioxide.—The yield was essentially the same as that shown above when 0.01 mole of tripotassium triazacyclohexanetrisulfonate was added to a solution of 0.0225 mole of stabilized liquid sulfur trioxide in 0.11 mole of absolute nitric acid, but the crude (198–201°) and the refined (204.5–204.8°) melting points were slightly better. However the violence of solution of sulfur trioxide in nitric acid (even at −40°) recommends the procedure with phosphorus pentoxide for laboratory use.

Summary

1. Molecular weight determinations by X-ray diffraction studies of the crystal and by freezing point determination of its aqueous solution show that when formaldehyde and potassium sulfamate react they form tripotassium 1,3,5-triazacyclohexane-1,3,5-trisulfonate rather than potassium methylenesulfamate.

2. This trimeric structure is confirmed by nitration studies since only the trimer, 1,3,5-trinitro-1,3,5-triazacyclohexane is produced in absence of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane.

TORONTO, CANADA RECEIVED FEBRUARY 4, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE]

C¹⁴ Tracer Studies in the Synthesis of Malonic Acid-2-C¹⁴ and Diethyl Malonate-2-C¹⁴ [1]

BY GUS A. ROPP

Although the isotope dilution method for determining the amount of each of several isotopically labeled components in a difficult mixture has been described,[2,3] little attention has been called to its particularly valuable application to determination of successive yields in a series of organic reactions where the scale is so small as to make isolation and identification of the successive products impossible. In the present examples, the syntheses of carbon-14 labeled malonic acid and diethyl malonate by independent methods are described.

In the first and most successful synthesis, a modification of the "Organic Syntheses"[4] procedure was used and the yields of products and of certain intermediates were determined by dilution of appropriate aliquots with the corresponding non-radioactive compounds and radioactive assay of purified derivatives. Potassium acetate-2-C¹⁴ having a millimolar[5] activity of 8 μc. was converted *via* bromoacetic and cyano-

(1) This document is based on work performed under Contract Number W-7405, eng. 26 for the Atomic Energy Project at Oak Ridge National Laboratory.

(2) Calvin, Heidelberger, Reid, Tolbert and Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, Appendix I.

(3) Keston, Udenfriend and Levy, THIS JOURNAL, **69**, 3151 (1947).

(4) Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 376.

(5) It was suggested by Dr. O. K. Neville that this term be used instead of "molar specific activity of 8 μc. per mmole."