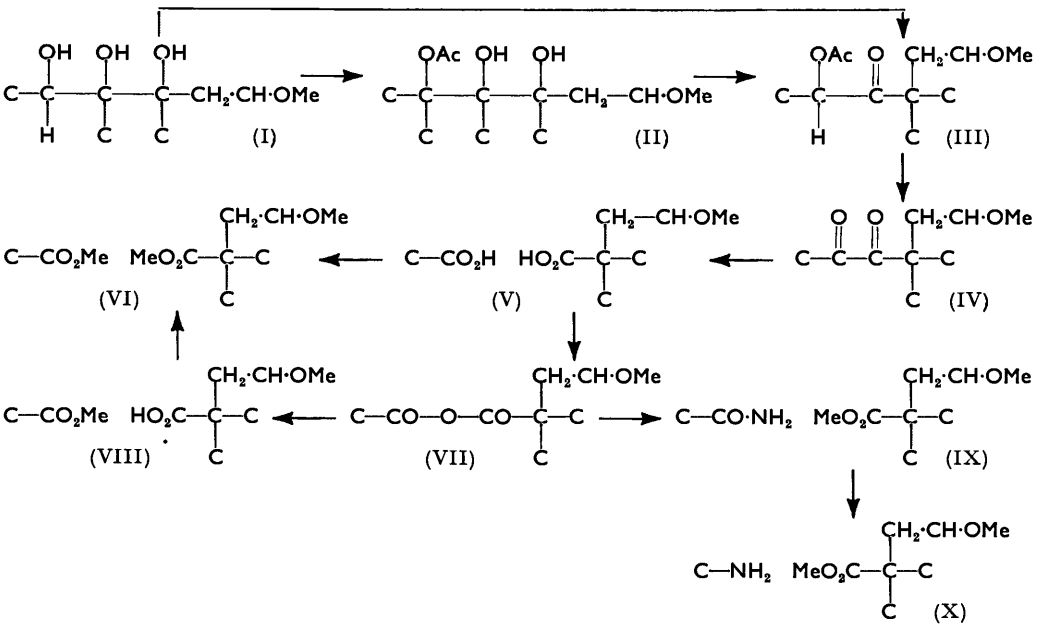
751. Aconitum *and* Delphinium *Alkaloids. Part III.* Some Rearrangements in the Delpheline and Lycoctonine Series. A Monobasic Dicarboxylic Acid.*

By R. C. Cookson and M. E. Trevett.

Acetyl chloride causes pinacolic dehydration of demethyleneoxodelpheline to an α-acetoxy-ketone that is converted *via* an α-diketone into a dicarboxylic acid. Although it undoubtedly contains two carboxyl groups, this acid titrates as a strong monobasic acid. On harsher treatment with acid further rearrangement occurs, giving an αβ-unsaturated ketone. Analogous rearrangements take place in the lycoctonine series.

Demethyleneoxodelpheline has been shown * to contain the group (I), which forms the secondary monoacetate (II) with acetic anhydride and pyridine. But treatment of the triol (I) with acetyl chloride caused dehydration as well as acetylation, with formation of a substance that formed no carbonyl derivatives under normal conditions but was recognised as a ketone by its characteristic absorption spectra, $\lambda_{max.}$ 293—294 mμ (ε 114) and $\nu_{max.}$ 1738 cm.$^{-1}$ (ketone and acetate superimposed, in Nujol). A choice amongst the various possible ways in which water might have been eliminated from the triol (I), either with or without rearrangement, was easily made when the pinacone acetate was found to be a secondary α-acetoxy-ketone.



Hydrolysis of the pinacone acetate gave an amorphous ketol, or mixture of ketols, that formed an isomeric acetate on re-acetylation, and was oxidised by chromic oxide in pyridine to a pale yellow, crystalline α-diketone. Thus the pinacone acetate must have the partial structure (III) and the α-diketone (IV).

The rather high frequencies (1758 and 1720 cm.$^{-1}$, in CS_2) of the C=O stretching vibrations of the α-diketone (IV) led us to consider that the diketone (IV) might be a *cyclo*pentanedione,[1] which would have required the three hydroxyl groups of the triol (I) to be attached

* Part II, *J.*, 1956, 3121.

[1] Cookson and Trevett, *Chem. and Ind.*, 1954, 1391.

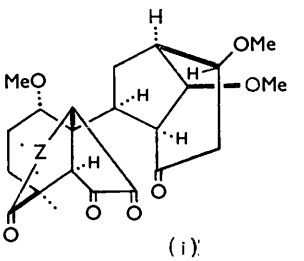
to the same *cyclo*pentane ring. But recent data [2] make it much more likely that it is a *cyclo*hexanedione formed from (I) by ring-expansion.

Unbridged *cyclo*hexanediones have their longest ultraviolet band [3,4] at about 350—380 mμ (in EtOH) and the two carbonyl-stretching bands,[3] which are not always resolved, between 1710 and 1730 cm.$^{-1}$ (in CS_2 or CCl_4). However, when the two carbonyl groups are kept coplanar by incorporation in a rigid, bridged ring, as in *bicyclo*[2 : 2 : 2]octane-2 : 3-dione, the ultraviolet maximum [2,5] is shifted to 478 mμ (strongest vibrational band in *cyclo*hexane solution: probably corresponding to about 460 mμ in EtOH) and the infrared bands [2,5] are shifted to 1730 and 1760 cm.$^{-1}$. In bridged *cyclo*pentanediones [2,6], such as *bicyclo*[2 : 2 : 1]heptane-2 : 3-dione,[2] the corresponding maxima are at about 470 mμ (EtOH) and at 1760 and 1770—1780 cm.$^{-1}$. The spectroscopic properties of the pinacone diketone (III) ($\lambda_{max.}$ 402 mμ; $\nu_{max.}$ 1720 and 1758 cm.$^{-1}$) * clearly point to a bridged *cyclo*hexanedione, although this evidence is not conclusive in view of the possibility of spectroscopic interaction between the functional groups. The α-diketone (IV) was inert to long boiling with acetic anhydride and sodium acetate, and did not show any other sign of enolising.

The carbonyl groups showed the hindrance usual in this series—for example, the diketone (IV) was unchanged by long treatment with *o*-phenylenediamine in boiling acetic acid—but when hydrogen peroxide was added to an alkaline solution of the diketone (IV) the colour rapidly faded, and a dicarboxylic acid (V) was formed. Presumably the small, almost linear, and strongly nucleophilic hydroperoxide anion can attack one of the carbonyl groups where larger reagents fail. The acid (V) gave the dimethyl ester (VI) with diazomethane and the cyclic anhydride (VII) with acetic anhydride. Although the acid (V) certainly contained two carbonyl groups, from its method of preparation and from the characteristic infrared spectra of its derivatives (VI) and especially (VII), it titrated in 50% ethanol as a remarkably strong *monobasic* acid (pK' 3·75). Methoxide opened the anhydride (VII) to form an acid ester (VIII) in which the stronger carboxyl was esterified, allowing the weaker one to be titrated normally (pK' 5·85). Diazomethane turned the acid ester (VIII) into the diester (VI), but the isomeric acid ester could not be obtained crystalline by partial hydrolysis of the latter.

If, as once seemed possible,[11] delpheline were a 1 : 2-amino-alcohol, the stronger carboxyl group in the acid (V) would have had the amide-nitrogen atom α to it, as in (A). The absence of such a group was demonstrated by opening the anhydride with ammonia to an amorphous amide-acid, converted by diazomethane into a crystalline amide-ester (IX). Treatment of the amide with hypobromite gave an amino-ester (X) that was

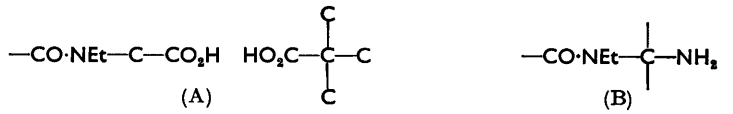
* The light absorption of the yellow *cyclo*hexanedione (IV) contrasts with that of the red *seco*-diketone [7] (i), a *cyclo*pentanedione ($\lambda_{max.}$ 490 mμ; $\nu_{max.}$ 1775 and 1755 cm.$^{-1}$), which absorbs at about 90 mμ longer wavelength in the ultraviolet and at substantially higher frequencies in the infrared. The long wavelength of the maximum of (i) compared with that of, say, camphorquinone (466 mμ) may be partly due to interaction with the adjacent amide group: cf. the orange 5 : 5-dihalogeno-3 : 3 : 4 : 4-tetramethyl*cyclo*pentane-1 : 2-dione,[8] the "bright raspberry-coloured" 2 : 2 : 5 : 5-tetramethyltetrahydro-3 : 4-dioxofuran,[9] and the "crimson-red" 5 : 5-dimethoxy-3 : 3 : 4 : 4-tetramethyl*cyclo*pentane-1 : 2-dione.[10] The last has $\lambda_{max.}$ 510 mμ.



(i)

[2] Alder, Schäfer, Esser, Krieger, and Reubke, *Annalen*, 1955, **593**, 23.
[3] Amongst others, Leonard and Mader, *J. Amer. Chem. Soc.*, 1950, **72**, 5388; Jones, Humphries, and Dobriner, *ibid.*, p. 956; Voser, Günthard, Heusser, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 2065.
[4] Richter, Schindler, and Reichstein, *ibid.*, 1954, **37**, 76, and later papers in that series.
[5] See also Naffa and Ourisson, *Bull. Soc. chim. France*, 1954, 1115.
[6] Vaughan and Peters, *J. Org. Chem.*, 1953, **18**, 382; Eastman and Selover, *J. Amer. Chem. Soc.*, 1954, **76**, 4118.
[7] Cookson and Trevett, *J.*, 1956, 3121.
[8] Ingold and Shoppee, *J.*, 1928, 365.
[9] Dupont, Dulou, and Lefort, *Bull. Soc. chim. France*, 1949, 789; Korobitsyna, Yuryev, and Nefedova, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 188.
[10] Shoppee, *J.*, 1936, 269.
[11] Cookson and Trevett, *Chem. and Ind.*, 1954, 1324; cf. *J.*, 1956, 2689.

stable to boiling concentrated hydrochloric acid. Had the group (B) been present it would surely have been hydrolysed.



(A) (B)

Acetyl chloride induced an analogous pinacolic dehydration of oxolycoctonine [12] and its derivatives to a pinacone, that on treatment with more strongly acidic reagents underwent a complex rearrangement with elimination of methanol and hydrolysis of a second methoxyl group to form an αβ-unsaturated ketone. Since Edwards and Marion [13] have independently discovered and investigated these two compounds, which they call " anhydrolycoctonam " and " lycoctamone," we include in the Experimental part of this paper only brief mention of some experiments that have not been duplicated. They could not, at that time, decide which carbon atom had migrated during the pinacol rearrangement, but the presence of the secondary hydroxyl group in demethyleneoxodelpheline (I) made the decision a simple one for us.

	$\Delta[M]_D$ [a]	$\lambda_{max.}$ in mμ (ε)	$\nu_{max.}$ in cm.$^{-1}$
Dehydroxymethyloxolycoctonine pinacone	−250° [b]	305 (83) [b]	1730, 1637 [c]
Acetyldemethyleneoxodelpheline pinacone	−140 [c]	293—4 (114) [b]	1738, 1636 [d]
Lycoctamone	+800 [b]	213 (12,300) [b]	1675, 1620 [c]
		243 (10,500)	
		306 (310)	
Delphelamone	+940 [c]	215 (11,300) [b]	1675, 1620 [c]
		243 (11,600)	
		314 (100)	

[a] $[M]_D$ of derivative minus $[M]_D$ of corresponding unrearranged glycol. [b] Ethanol. [c] Chloroform. [d] Nujol.

In strongly acid media demethyleneoxodelpheline pinacone acetate (III) developed an ultraviolet maximum at 245 mμ (ε 10,000); treatment of oxodelpheline, *iso*oxodelpheline, or demethyleneoxodelpheline with, for example, boiling hydrochloric acid led to a crystalline αβ-unsaturated ketone which we call delphelamone, for it is, we shall show, the analogue of lycoctamone. The Table, summarising the optical properties of the products of rearrangement in the lycoctonine and delpheline series, brings out the very close resemblance between the two series.

Dehydration of oxolycoctonine (XI; R = Me, X = OH) must give the pinacone (XII; R = Me, X = OH): the stereochemistry is very favourable for such a rearrangement. If demethyleneoxodelpheline has the analogous structure [7] (XI; R = X = H), then the pinacone acetate (III) must have the complete structure (XII; R = Ac, X = H), and the isomeric acetate from hydrolysis and re-acetylation is probably (XIII), which appears to be the most stable of the four possible ketol acetates. The nature of the delphelamone and lycoctamone rearrangements will be discussed later.

On the basis of structure (XII; R = Ac, X = H) for the pinacone acetate (III), the dicarboxylic acid (V) would be (XIV).* The drawing (XV) illustrating the environment of the two carboxyl groups in this dicarboxylic acid shows how near they are held to one another by the rigid ring-system. The anion-acid will then be stabilised by an exceptionally strong internal hydrogen bond (XVI), while the dianion will be correspondingly destabilised by strong electrostatic repulsion and by hindrance to external hydrogen bonding and solvation.[14]

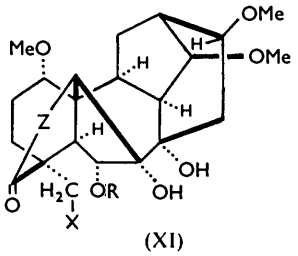
cis-Caronic acid [15] (3 : 3-dimethyl*cyclo*propane-1 : 2-*cis*-dicarboxylic acid) with p*K*

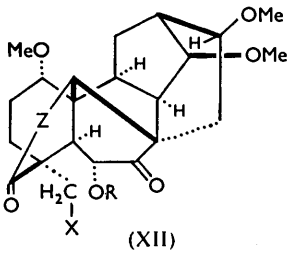
* Although one ring used for configurational reference is broken, to avoid confusion formula (XIV) is projected in the same way as the hexacyclic formulæ, so that the two carboxyl groups and the other carbon atoms of the former seven-membered ring and the six- and five-membered rings linearly condensed with it are taken as the reference system (see *J.*, 1956, 3124).

[12] Ref. 7, footnote, on p. 3124.
[13] Edwards and Marion, *Canad. J. Chem.*, 1952, **30**, 627; 1954, **32**, 708.

values in water of 2·34 and 8·31 seems to provide the closest analogy for the behaviour of the dicarboxylic acid * (XIV).

In (XI)—(XIV), Z = NEt


(XI)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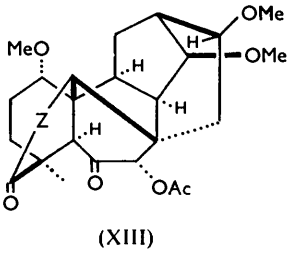
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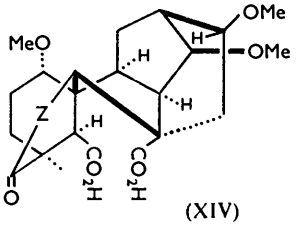
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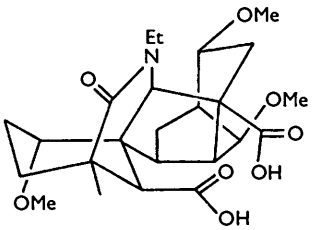
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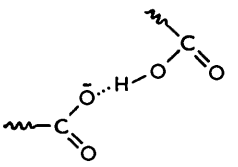
(XVI)

Experimental

Unless otherwise stated, rotations were measured in $CHCl_3$, ultraviolet spectra in EtOH, and apparent dissociation constants in ethanol–water (1 : 1 by vol.).

Treatment of Demethyleneoxodelpheline with Acetyl Chloride.—Demethyleneoxodelpheline (112 mg.) in acetyl chloride (5 ml.) was boiled for 6 hr. The product, isolated with chloroform (and kept away from alkali), crystallised from aqueous ethanol to give needles of the *pinacone acetate* (III) (50 mg.), m. p. 214—218°, $[\alpha]_D$ −15·5°, $\lambda_{max.}$ 293—294 mμ (ε 114), $\nu_{max.}$ 1738 (s) and 1636 cm.$^{-1}$ (Nujol) (Found : C, 65·5; H, 8·1; N, 2·8; OMe, 18·9. $C_{26}H_{37}O_7N$ requires C, 65·7; H, 7·9; N, 2·95; 3OMe, 19·5%). This acetate was changed by treatment with such alkaline reagents as alumina or potassium carbonate.

Isomerisation of the Pinacone Acetate.—The acetate (III) (186 mg.) in ethanol (6 ml.) and N-sodium hydroxide (10 ml.) was boiled for 2 hr. The oil (156 mg.), extracted with chloroform, was dissolved in acetyl chloride (5 ml.), left overnight, and then boiled for ½ hr. The resulting isomeric *acetate* (111 mg.) separated from aqueous ethanol in cube-like crystals, m. p. 217—219°, $[\alpha]_D$ −55°, $\lambda_{max.}$ 293 mμ (ε 45), $\nu_{max.}$ 1756, 1728, and 1654 cm.$^{-1}$ (CS_2) (Found : C, 65·9; H, 7·8; N, 3·1%).

The α-Diketone.—The oily ketol from hydrolysis of the pinacone acetate (III) (450 mg.), as above, was oxidised with chromic oxide (450 mg.) in pyridine (9 ml.) at room temperature overnight. Crystallisation of the product from aqueous ethanol gave pale yellow needles of the α-diketone (IV), m. p. 212—215°, $[\alpha]_D$ −72°, $\lambda_{max.}$ 402 mμ (ε 53), infl. 290 mμ (ε 150), $\nu_{max.}$ 1758, 1720, and 1658 (CS_2) (Found : C, 66·7; H, 7·7; N, 3·3. $C_{24}H_{33}O_6N$ requires C, 66·8; H, 7·7; N, 3·25%).

The Monobasic Dicarboxylic Acid.—Hydrogen peroxide (" 100-vol."; 15 ml.) was added to a

* Though it is obviously not a close analogue of the saturated dicarboxylic acid (XIV) we did titrate under the same conditions naphthalene-1 : 8-dicarboxylic acid, which has its two carboxyl groups close together. It titrated normally, showing an equivalent weight of half the molecular weight, and apparent p*K*'s of about 5·4 and 7·3.

[14] Bird and Cookson, *Chem. and Ind.*, 1955, 1479.

[15] Jones and Soper, *J.*, 1936, 133; see also Brown, McDaniel, and Häfliger in Braude and Nachod's " Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, 1955, p. 632; Cardwell, Dunitz, and Orgel, *J.*, 1953, 3740.

solution of the α-diketone (IV) (200 mg.) in 2% potassium hydroxide in methanol (35 ml.). An hour later the acidic product was separated and crystallised from ethyl acetate as a white, microcrystalline powder (160 mg.). This *dicarboxylic acid* (V) had m. p. 206° (decomp.), $[\alpha]_D$ −22°, $\nu_{max.}$ 1700 and 1645 (CS_2), or 1695 and 1646 cm.$^{-1}$ (Nujol), p*K*′ 3·75 [Found : C, 61·8; H, 7·7; N, 3·3; OMe, 19·5%; equiv., 468 (phenolphthalein), 464 (electrometrically). $C_{24}H_{35}O_8N$ requires C, 61·9; H, 7·6; N, 3·0; 3OMe, 20·0%; *M*, 466].

The *dimethyl ester* (VI), made with diazomethane in methanol–ether, crystallised from aqueous acetone in prisms, m. p. 164—165°, $[\alpha]_D$ −36°, $\nu_{max.}$ 1728 and 1640 cm.$^{-1}$ (CS_2) (Found : C, 63·2; H, 7·9; N, 2·8; OMe, 31·6. $C_{26}H_{39}O_8N$ requires C, 63·3; H, 8·0; N, 2·8; 5OMe, 31·4%).

The Dicarboxylic Anhydride.—The dicarboxylic acid (V) (94 mg.) in acetic anhydride (10 ml.) was boiled for 6 hr. The solvent was removed under reduced pressure and the residue crystallised from acetone–ether as pyramids of the *anhydride* (VII) (83 mg.), m. p. 248—254°, $[\alpha]_D$ −45°, $\nu_{max.}$ 1800, 1758, and 1660 cm.$^{-1}$ (CS_2) (Found : C, 64·1; H, 7·45; N, 3·2. $C_{24}H_{33}O_7N$ requires C, 64·4; H, 7·4; N, 3·1%).

Hydrolysis of the anhydride with boiling 2N-sodium hydroxide gave a quantitative yield of the dicarboxylic acid (V), m. p. and mixed m. p. 201—203°.

Methanolysis of the Dicarboxylic Anhydride.—A solution of the anhydride (50 mg.) in 5% methanolic sodium methoxide (5 ml.) was left at room temperature overnight. The acidic product was isolated with chloroform and crystallised from acetone–ether to yield the *acid ester* (VIII) (38 mg.), m. p. 191—192°, $[\alpha]_D$ −30°, p*K*′ 5·85 (Found : C, 62·4; H, 8·0; N, 3·1; OMe, 26·0. $C_{25}H_{37}O_8N$ requires C, 62·6; H, 7·8; N, 2·9; 4OMe, 25·7%).

Diazomethane turned the half-ester into the dimethyl ester (VI), m. p. and mixed m. p. 161—162°.

The Methyl Ester-amide.—Dry ammonia was bubbled through a boiling solution of the anhydride (50 mg.) in dioxan (30 ml.) and benzene (30 ml.). The acidic product, isolated with chloroform, did not crystallise, but treatment with diazomethane gave the *methyl ester-amide* (IX) which crystallised from ether in needles (30 mg.), m. p. 228—229°, $[\alpha]_D$ −5·5°, $\nu_{max.}$ 1728, 1670, and 1615 (primary amide), and 1630 cm.$^{-1}$ (lactam) ($CHCl_3$) (Found : C, 62·9; H, 8·1; N, 5·6. $C_{25}H_{38}O_7N_2$ requires C, 62·7; H, 8·0; N, 5·85%).

The Methyl Ester-nor-amine.—A solution of the methyl ester-amide (23 mg.), potassium hydroxide (14 mg.), and bromine (10 mg.) in dioxan (1 ml.) and water (5 ml.) was left at room temperature for 1 hr. (The colour faded in about 5 min.) After the solution had then been warmed to 50° for 30 min. the product was extracted with chloroform and crystallised from ether–benzene, to provide the *methyl ester-nor-amine* (X) (15 mg.), m. p. 184—187° (Found : C, 64·3; H, 8·7; N, 6·1. $C_{24}H_{38}O_6N_2$ requires C, 64·0; H, 8·5; N, 6·2%).

The amine (X) was recovered almost quantitatively from solution in concentrated hydrochloric acid at room temperature after 20 hr., in boiling concentrated hydrochloric–acetic acid (1 : 1) after 2 hr., and in boiling concentrated hydrochloric acid after 1 hr.

Delphelamone.—*iso*Oxodelpheline (22 mg.) in dioxan (1 ml.) and concentrated hydrochloric acid (2 ml.) was boiled for 10 min. Isolation with chloroform and crystallisation from ethyl acetate–*cyclo*hexane gave *delphelamone* (8 mg.), m. p. 247° (decomp.), $[\alpha]_D$ +281°, $\lambda_{max.}$ 215 (ε 11,300), 243 (ε 11,600), and 314 mμ (ε 100), $\nu_{max.}$ 1675 and 1620 cm.$^{-1}$ ($CHCl_3$) (Found : C, 66·75; H, 7·3; OMe, 7·45. $C_{22}H_{29}O_5N,\frac{1}{2}H_2O$ requires C, 66·65; H, 7·6; 1OMe, 7·8%).

*iso*Oxodelpheline (25 mg.), heated on a steam-bath for 1 hr. in formic acid (8 g.) and phosphoric acid (2 g.), gave a gum (25 mg.), having $\lambda_{max.}$ 245 mμ (ε 10,000), which on crystallisation yielded delphelamone, m. p. 238—240°, not depressed by the first sample. Treatment of oxodelpheline with hydrochloric acid or with phosphoric and formic acids also produced delphelamone.

Acetylation of Lycoctonine.—With acetic anhydride and pyridine or with acetic anhydride and a trace of sulphuric acid at room temperature lycoctonine formed a gummy monoacetate, which gave a crystalline *perchlorate*, m. p. 194—195° (decomp.) after recrystallisation from ethanol–ethyl acetate (Found : C, 53·1; H, 7·4. $C_{27}H_{44}O_{12}NCl$ requires C, 53·15; H, 7·3%).

Acetyl-lycoctonine perchlorate regenerates lycoctonine on alkaline hydrolysis. The crystalline acetyl derivative, characterised only by its acetyl value, made by long reaction of lycoctonine with acetyl chloride [16] may be a product of rearrangement : the published acetyl determinations agree better with values expected for an anhydro-acetate.

[16] Suginome and Ohno, *J. Fac. Science, Hokkaido Univ.*, 1950, Ser. III, **4**, 36.

Acetyloxolycoctonine Pinacone.—This substance, the anhydrolycoctonam acetate of Edwards and Marion,[13] was most conveniently made from methyl-lycoconitine hydriodide by conversion into the amorphous free base, oxidation with potassium permanganate in acetone to the amorphous oxo-derivative, and hydrolysis to oxolycoctonine, which without crystallisation was treated with acetyl chloride. Oxolycoctonine pinacone, prepared by hydrolysis of the acetate, agreed in its physical properties with those reported by Edwards and Marion,[13] and in CS_2 had $\nu_{max.}$ 1730 and 1630 cm.$^{-1}$.

Lycoctamone.—Oxolycoctonine pinacone (734 mg.) was shaken with a concentrated solution of zinc chloride[17] (14 ml. of a solution of 60 g. of $ZnCl_2$ in 20 ml. of 12% hydrochloric acid) at room temperature. Dissolution was complete after about 1 hr. and after 3·5 hr. the solution was diluted with water and extracted with chloroform, which was filtered through alumina to remove a trace of yellowish material that was difficult to get rid of by crystallisation. Large, cube-like crystals of lycoctamone separated from aqueous ethanol, and had m. p. 220—225°, $[\alpha]_D$ +257° (EtOH), $\lambda_{max.}$ 213 (ε 12,300), 243 (ε 10,500), and 306 mμ (ε 310), $\nu_{max.}$ 1660 and 1608 cm.$^{-1}$ (Nujol) (Found: C, 63·5, 63·55; H, 7·7, 7·6; OMe, 15·0; loss at 110° *in vacuo*, 4·1. Calc. for $C_{23}H_{31}O_6N,H_2O$: C, 63·4; H, 7·6; 2OMe, 14·3; $1H_2O$, 4·1%).

Oxolycoctonine pinacone (88 mg.), dissolved in 75% perchloric acid (1 ml.), was left at room temperature for 4·5 hr. The resulting gum crystallised under ether as lycoctamone (43 mg.), m. p. 210—215° (sintering at 208°, clear liquid at 219°) after recrystallisation from aqueous ethanol.

Lycoctamone acetate, made with acetic anhydride and pyridine and crystallised from aqueous ethanol, had m. p. 223—225°, $[\alpha]_D$ +215° (EtOH), $\nu_{max.}$ 1748, 1684, and 1640 (CS_2), or 1748, 1674, and 1622 cm.$^{-1}$ (Nujol) (Found: C, 65·4; H, 7·5; N, 3·25. Calc. for $C_{25}H_{33}O_7N$: C, 65·3; H, 7·2; N, 3·05%).

Lycoctamone (53 mg.) and 2 : 4-dinitrophenylhydrazine (39 mg.) in ethanol (2 ml.) and concentrated hydrochloric acid (4 drops) were boiled for 1 hr. The product, extracted with ethyl acetate, was adsorbed on to alumina from benzene. Benzene and ethyl acetate eluted negligible amounts of orange products, but chloroform removed 74 mg. that crystallised from aqueous methanol. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate–*cyclo*hexane in bright red blades, m. p. 236—237°, $\lambda_{max.}$ 377 mμ (ε 28,100) in $CHCl_3$ (Found: C, 58·1; H, 6·0; N, 11·6. $C_{29}H_{35}O_9N_5$ requires C, 58·3; H, 5·9; N, 11·7%).

Oxolycoctonine Pinacone Aldehyde.—The pinacone (100 mg.) and chromic oxide (100 mg.) in pyridine (2 ml.) were left overnight. Extraction with chloroform and crystallisation from aqueous ethanol gave the corresponding *aldehyde* (60 mg.), m. p. 156—157°, $[\alpha]_D$ +54° (EtOH), $\lambda_{max.}$ 305 mμ (ε 117) (Found: C, 64·8; H, 7·5; N, 3·1. $C_{25}H_{35}O_7N$ requires C, 65·05; H, 7·6; N, 3·0%).

Lycoctamone Aldehyde.—Lycoctamone (150 mg.) and chromic oxide (150 mg.) in pyridine (3 ml.) were left for 2 hr. After crystallisation from ethyl acetate–*cyclo*hexane the resulting *aldehyde* (112 mg.) had m. p. 210—214°, $[\alpha]_D$ +282°, $\lambda_{max.}$ 213 (ε 12,250), 245 (ε 11,100), and 316 mμ (ε 57) (Found: C, 66·3; H, 7·2; N, 3·5. $C_{23}H_{29}O_6N$ requires C, 66·5; H, 7·0; N, 3·4%).

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[17] Cf. Jacobs and Pelletier, *J. Amer. Chem. Soc.*, 1954, **76**, 161, and earlier papers.