Mass Spectra.—An Hitachi Perkin-Elmer RMU-6D double focussing mass spectrometer was used, operating at 75 eV, with an inlet and source temperature of *ca.* 215°.

Nuclear Magnetic Resonance Spectra.—A Varian HA-100 spectrometer with Hewlett-Packard audio oscillator Models 200 CD and 200 AB was used. The samples were run in benzene-d_6 and deuterio chloroform, with tetramethylsilane as internal standard.

Isolation Procedure.—*Stevia serrata* was collected in September 1971 south of México City. A 4-kg portion of dried whole plant was extracted with 25 l. of warm methanol. The extract was filtered and concentrated to 2 l., then 1 l. of water was added and extracted, first with 1 l. of hexane, which was discarded, and then with 2 l. of chloroform. The chloroform extract was washed with water and concentrated to dryness, giving 200 g of a syrupy brown oil. The part soluble in AcOEt 10/B90, 180 g, was chromatographed on silica gel (packed in AcOEt 10/B90). The column was successively eluted, starting with 3 l. of AcOEt 10/B90, and increasing the amount of AcOEt in the solvent mixture in the following fashion: 3 l. (40/60), 4 l. (60/40), 2 l. (100); fractions close to 300 ml were taken. Fractions 20–40 were combined and evaporated to dryness, and the residue, 123 g of syrup, was redissolved in AcOEt 5/B95 and chromatographed in 2 kg of alumina. The column was packed in AcOEt 5/B95 and successively eluted, taking fractions of about 500 ml, first 5 l. (AcOEt 5/B95), 5 l. (AcOEt 10/B90), 20 l. (AcOEt 20/B80), 7 l. (AcOEt 40/B60), and finally 2 l. (AcOEt 90/MeOH 10). All fractions were monitored by tlc. Fractions 32–37 were joined and christinine, 250 mg, crystallized out in ethyl acetate–hexane. One recrystallization from acetone–diisopropyl ether yielded pure christinine (1): mp 164–165°; $[\alpha]_D$ + 19.72° (*c* 3.65, $CHCl_3$); ir ($CHCl_3$) 1775, 1730, 1360, 1000, 940 cm^{-1}; uv max (95% EtOH) 215 nm (ϵ 2270); mass spectrum (75 eV) *m/e* (rel intensity) 304 (M^+ − 60), 244 (45), 202 (64), 200 (74), 185 (47), 171 (77), 159 (100), 157 (63), 141 (70), 131 (85), 129 (77), 128 (82), 115 (71), 105 (24), 91 (39), 60 (31), 45 (20), 43 (30).

Anal. Calcd for $C_{19}H_{24}O_7$: C, 62.62; H, 6.64; O, 30.76. Found: C, 62.54; H, 6.61; O, 30.47.

Registry No.—1, 38555-39-4.

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Total Synthesis of the Pavinane Alkaloid Platycerine[1]

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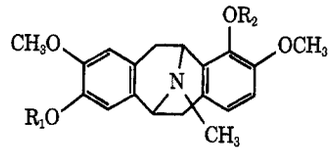
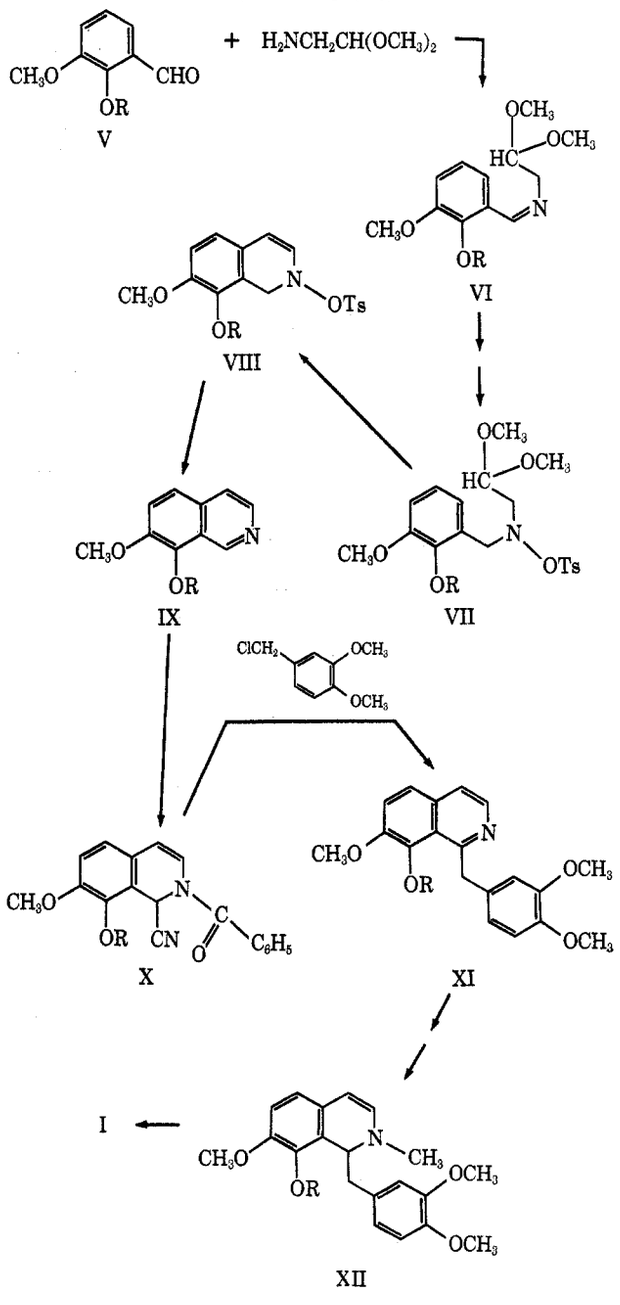
The alkaloid platycerine (I) was first isolated[2] from *Argemone platyceras* Link et Otto. and it was later shown[3] that methylation converted platycerine to *O,O*-dimethylmunitagine (II). II in turn had been prepared[4] by methylation of munitagine (III), whose structure rested[4] upon spectrographic and degradative evidence. Platycerine had also been isolated[5] from *A. gracilenta* Greene and structure I proposed[5] on the basis of its preparation by methylation of munitagine and its mass spectral fragmentation pattern. However, the alternate structure IV for platycerine remained an outside possibility and hence we have synthesized I as final proof of structure.



I, $R_1 = CH_3$; $R_2 = H$
II, $R_1 = R_2 = CH_3$
III, $R_1 = R_2 = H$
IV, $R_1 = H$; $R_2 = CH_3$

Our synthesis was accomplished by means of Scheme I and yielded (±)-platycerine identical with the natural

SCHEME I
(R = $CH_2C_6H_5$)



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material (except for optical rotation), and hence structure I for platycerine is confirmed.

Experimental Section

2-Benzyloxy-3-methoxybenzaldehyde (V) was prepared by benzylation of *o*-vanillin according to the method of Uff.[6a] V was obtained in 80% yield as colorless needles (crystallized from ether), mp 44° (lit.[6b] mp 44.0–44.5°).

7-Methoxy-8-benzyloxyisoquinoline (IX).—An adaptation of the method of Jackson and Stewart[7] was used. Intermediates to IX were isolated but were not rigorously purified at each step. A mixture of V and 10% excess aminoacetaldehyde dimethyl acetal was heated in benzene at reflux with a Dean–Stark trap until the calculated amount of water was collected. Excess amino acetal was removed by washing, and distillation *in vacuo* left the product Schiff's base VI as a yellow oil. VI was quantitatively reduced to the amine in ethanol with 1% by weight PtO_2 in a Parr apparatus at 50 psi hydrogen. The amine was converted to the tosylate VII in good yield with *p*-toluenesulfonyl chloride in pyridine. VII (0.1 mol) was dissolved in a solution of 100 ml of peroxide-free dioxane and 15 ml of 6 *M* HCl and the solution was heated at reflux in the dark until tlc showed complete disappearance of VII. The reaction mixture was washed with water and the solvent was removed *in vacuo* to leave VIII as a brown oil. VIII was stirred for several hours in a solution of potassium *tert*-butoxide in *tert*-butyl alcohol under gentle heat. After the mixture had cooled, benzene and water were added and the benzene layer was washed several times with additional water. The benzene layer was dried and the solvent was evaporated to leave a red oil, which was purified by Florisil column chromatography to yield red needles of IX, mp 188° (lit.[6] mp 185–188°), in 60% yield from V.[8]

***N*-Benzoyl-8-benzyloxy-1,2-dihydro-7-methoxyisoquinoline-1-carbonitrile** (X).—To 75 ml (0.15 mol) of an aqueous solution of KCN in an ice-cold three-neck flask fitted with a mechanical stirrer, addition funnel, and condenser was added IX (13 g, 0.05 mol). The mixture was stirred until a fine suspension of IX in the solution was obtained. Benzoyl chloride (0.1 mol) was then added dropwise with stirring. Stirring was continued until the Reissert compound X separated as a tan solid. This was filtered off and recrystallized from ethanol to yield 65% X as a white solid, mp 135° (lit.[6a] mp 135°).

1-(3,4-Dimethoxybenzyl)-7-methoxy-8-benzyloxyisoquinoline (XI).—The nitrile X (12 g in 100 ml of DMF at 0°) was treated under nitrogen with a threefold excess of NaH, and then a twofold excess of 3,4-dimethoxybenzyl chloride in 50 ml of DMF was added. The mixture was stirred overnight and then ethanol was added to destroy the excess NaH. Benzene and water were added and the benzene layer was separated and washed again with water and finally with 6 *M* HCl. The acidic layer was made basic with NaOH and extracted with $CHCl_3$. The $CHCl_3$ layers were combined, dried over K_2CO_3, and evaporated to yield XI in 80% yield. Recrystallization from ethanol gave XI as a white solid: mp 117°; nmr ($CDCl_3$) δ 8.2 (d, 1, H on C_3), 7.7–6.6 (m, 6, aromatic H), 5.0 (s, 2, $OCH_2C_6H_5$), 4.88 (s, 2, CH_2), 3.93 (s, 3, OCH_3), 3.70 (s, 3, OCH_3), 3.60 (s, 3, OCH_3).

Anal. Calcd for $C_{26}H_{25}NO_4$: C, 75.08; H, 5.97; N, 3.29. Found: C, 75.16; H, 6.06; N, 3.37.

(±)-Platycerine (I).—The isoquinoline XI (3 g) was converted to the methiodide by heating in a mixture of 15 ml of CH_3I and CH_3OH. The solvents were removed *in vacuo* and the yellow solid which was obtained was dried and then added to a slurry of $LiAlH_4$ (0.75 g) in dry ether. The slurry was stirred for 3 hr and the excess hydride was decomposed by the addition of wet ether and a saturated solution of sodium potassium tartrate. The ether layer was separated and evaporated to yield the 1,2-dihydroisoquinoline XII as a yellow oil. To XII was added 25 ml of 7:5 $HCOOH$–H_3PO_4 and the solution was heated at reflux until all XII had disappeared as evidenced by tlc. The solution was then diluted with water and washed with $CHCl_3$. The aqueous layer was made basic to pH 8 with NaOH solution and extracted with $CHCl_3$. The $CHCl_3$ layers were combined, dried over K_2CO_3, and evaporated to yield a crude oil shown by tlc and nmr to be the desired I in 60–70% yield. Preparative layer chromatography yielded a sample of pure (±)-platycerine (I) whose $CHCl_3$ ir, $CDCl_3$ nmr, cyclohexane uv, and tlc R_f value (0.55 using silica gel G and 3:2 benzene–methanol) were identical with those of the natural alkaloid.[4]

Registry No.—I, 38863-79-5; V, 2011-06-5; VI, 38868-50-7; VII, 38868-51-8; VIII, 38868-52-9; IX, 36454-41-8; X, 38868-54-1; XI, 38868-55-2.

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(8) We are indebted to Mr. John Lawson for technical assistance in this preparation.

The Photocycloaddition of Diphenylacetylene to 1,5-Cyclooctadiene

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It is known that diphenylacetylene photoreacts with tetramethylethylene[1] and cyclic vinyl ethers[2] to give the cyclobutene derivatives. In an earlier paper[3] we reported the photocycloaddition of diphenylacetylene to norbornadiene, in which the products that were considered to be formed by the further reactions of the intermediate cyclobutene were obtained in contrast to the above reactions. In order to observe the behavior of diphenylacetylene in other dienes, we photolyzed a solution of diphenylacetylene in 1,5-cyclooctadiene. The reaction mixture was irradiated for 40 hr through a Pyrex filter with a high-pressure mercury lamp. Chromatography on silica gel gave only one product, **1** (72%).

Elemental analysis and the mass spectrum (M^+ 286) indicated that this product was a 1:1 adduct of diphenylacetylene and 1,5-cyclooctadiene. The nmr spectrum showed no signals in the vinyl region, and was very simple, indicating that this product has the symmetrical structure. The possible structure for this product is **1** or **2**, whose type of structure was assigned to the photoadduct of acetylenedicarboxylic acid and 1,4-cyclohexadiene.[4,5]

This product was stable on heating for 1 hr at 47° in 2 *N* sulfuric acid, where norcarane completely decomposed,[6] and the signal at δ 3.04 is at too low field to be assigned to the ring protons of cyclopropanes.[7] Structure **1** is compatible with these properties, but structure **2** is not. Thus, this product was assigned the structure 9,10-diphenyltetracyclo[6.2.0.0^{4,10}.0^{5,9}]-decane.

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