is then used to correct for exchange or intermolecular transfer. Predicting the distribution for the intermolecular transfer involves the following process (example experiment 1): (a) remove one atom of D from all deuterated species to give 28.4% D_2 + 12.4% D_1 + 59.2% D_0 and 42.6% D which is being transferred, (b) exchange 47% of the deuterium which has been removed for H (the hydrogen being transferred is now 22.6% D and 77.4% H), (c) recombine this H/D mixture statistically with the mixture of acceptor molecules from a to give 28.4% × 22.6% = 6.4% D_3, 28.4% × 77.4% = 22.0% D_2, 12.4% × 22.6% = 2.8% D_2, 12.4% × 77.4% = 9.6% D_1, 59.2% × 22.6% = 13.4% D_1, and 59.2% × 77.4% = 45.8% D_0, or a predicted distribution of 6.4% D_3, 24.8% D_2, 23.0% D_1, and 45.8% D_0. This prediction is obviously only very approximate since it assumes that the final ratio of labeled to unlabeled chanoclavine-I molecules is the same as that throughout the experiment. The prediction of the deuterium distribution for the case of intermolecular transfer and loss of one hydrogen from C-17 involves the same process using the figures obtained after correcting chanoclavine-I for loss of one hydrogen from C-17. Alternatively, the figures for the intermolecular transfer case can be used and corrected for loss of one atom of deuterium, giving a somewhat different set of numbers. Obviously, the number of assumptions inherent in these estimations is too great to allow prediction of accurate figures and the range covered by these two modes of calculation is therefore given.

In experiments 6 and 7 the prediction of the range of double labeled molecules expected is based on the following consideration. The minimum value follows from the assumption that the isotope distribution in chanoclavine-I was constant throughout the experiment. Single labeled chanoclavine-I species consist of ^{13}C and D molecules in a ratio of 43:50, i.e., in experiment 6 of 19.4% ^{13}C and 22.6% D. With a tritium retention of 65%, of the deuterium present 7.9% will exchange and the remaining 14.7% will statistically combine with 80.6% ^{12}C and 19.4% ^{13}C molecules to give 2.9% molecules containing ^{13}C and D. The other extreme follows from the assumption that all the labeled alkaloid is formed at a different time than unlabeled alkaloid from endogenous mevalonate. In this case there is no dilution of the precursor and therefore 65% of the deuterium of mevalonate (i.e., 32.5% D) would be distributed between 57% ^{12}C and 43% ^{13}C molecules to give 43% × 32.5% = 14% molecules containing ^{13}C + D.

Isolation, Gas Chromatography–Mass Spectrometry, and Structures of New Alkaloids from *Erythrina folkersii* Krukoff and Moldenke and *Erythrina salviiflora* Krukoff and Barneby[1]

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Abstract: We have developed a method for routine analysis of the *Erythrina* alkaloids to facilitate chemotaxonomic studies on species of *Erythrina*. The crude alkaloid mixtures are resolved and identified as their trimsyl (trimethylsilyl) derivatives by combined gas chromatography–mass spectrometry. We report here the salient gas chromatographic and mass spectral characteristics of the trimsyl derivatives of alkaloids from *E. folkersii* Krukoff and Moldenke and *E. salviiflora* Krukoff and Barneby. We also describe the isolation of three new *Erythrina* alkaloids—erysoline (5), erythravine (8), and erysosalvine (12)—and the isolation of erysotine (11) and erysotinone (17) for the first time from a natural source. Two more new *Erythrina* alkaloids–erysoflorinone and erysosalvinone (16 and 18)—have been characterized by gas chromatography–mass spectrometry as their trimsyl derivatives.

The *Erythrina* alkaloids[2] have been the subject of active investigation in recent years with respect to biosynthesis,[3] identification of known and new alkaloids,[4] mass spectrometric behavior,[5] and total synthesis.[6] Our own efforts have been directed toward a

(1) Presented in part at the 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, Ga., May 1971, Paper F7, and at the 8th International Symposium on the Chemistry of Natural Products, IUPAC, New Delhi, India, Feb 1972, Abstract A31.

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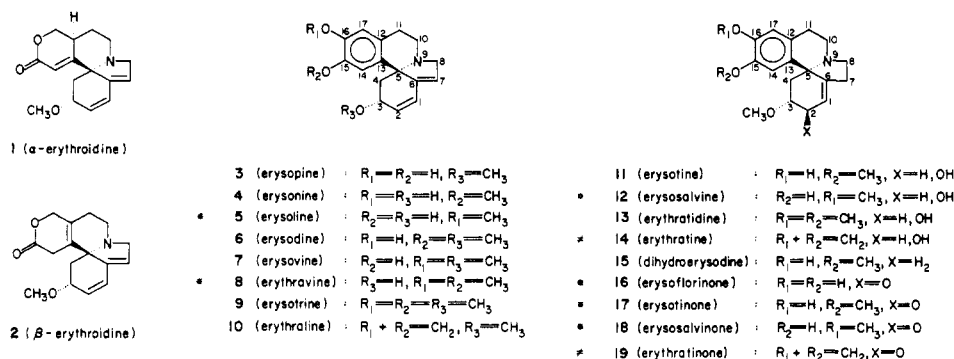
1 (α-erythroidine)

2 (β-erythroidine)

3	(erysopine)	:	$R_1=R_2=H, R_3=CH_3$
4	(erysonine)	:	$R_1=R_3=H, R_2=CH_3$
* 5	(erysoline)	:	$R_2=R_3=H, R_1=CH_3$
6	(erysodine)	:	$R_1=H, R_2=R_3=CH_3$
7	(erysovine)	:	$R_2=H, R_1=R_3=CH_3$
* 8	(erythravine)	:	$R_3=H, R_1=R_2=CH_3$
9	(erysotrine)	:	$R_1=R_2=R_3=CH_3$
10	(erythraline)	:	$R_1 + R_2=CH_2, R_3=CH_3$

11	(erysotine)	:	$R_1=H, R_2=CH_3, X=H, OH$
12	(erysosalvine)	:	$R_2=H, R_1=CH_3, X=H, OH$
13	(erythratidine)	:	$R_1=R_2=CH_3, X=H, OH$
* 14	(erythratine)	:	$R_1 + R_2=CH_2, X=H, OH$
15	(dihydroerysodine)	:	$R_1=H, R_2=CH_3, X=H_2$
* 16	(erysoflorinone)	:	$R_1=R_2=H, X=O$
* 17	(erysotinone)	:	$R_1=H, R_2=CH_3, X=O$
* 18	(erysosalvinone)	:	$R_2=H, R_1=CH_3, X=O$
* 19	(erythratinone)	:	$R_1 + R_2=CH_2, X=O$

Figure 1. Erythrina alkaloids: (*) new alkaloids isolated or identified in the present study; (≠) alkaloids other than those found in the present study.

comprehensive investigation of the alkaloidal composition of a large and diverse collection of *Erythrina* species,[7] with the treble goals of developing the combined technique of gas chromatography–mass spectrometry (gc–ms) as a tool for effecting complete characterization of the alkaloids in a plant species or genus and evaluating its utility in that capacity; of identifying new alkaloids by gc–ms and assigning structures to them; and of employing the alkaloidal compositions established for individual species as a chemotaxonomic guide within a plant genus.

We have now investigated a number of species of *Erythrina* by gc–ms and describe here the methodology developed, which has been modified from that employed in our extensive investigations of the *Ormosia* alkaloids.[8] We also report our results with the species *E. folkersii* Krukoff and Moldenke and *E. salviiflora* Krukoff and Barneby. The alkaloids of *E. folkersii* were investigated earlier[9] and the present results can be compared with those reported from the Folkers study. The alkaloids of *E. salviiflora* have not been reported previously; remarkably, they include three new *Erythrina* alkaloids and two not found previously in nature.

Results and Discussion

Structures of the *Erythrina* alkaloids found in the present investigation (and a few others) are shown in Figure 1. As seen there, most of the alkaloids encountered contain at least one hydroxyl group, and it was therefore necessary to improve their volatility in order to apply the combined gc–ms technique to their identification. This was achieved by conversion of the hydroxylic components to their trimsyl (trimethylsilyl) derivatives, which were stable on packed glass gc columns containing OV-17. The conditions employed[10] resolved

isomeric pairs resulting from reversed positions of methoxy and trimsyloxy substituents.

In order to identify the gas chromatographically separated components, the gas chromatograph was interfaced with a low-resolution mass spectrometer, *via* a two-stage Watson–Biemann molecular separator. Using this system, there was no loss in gas chromatographic resolution, as judged from a comparison of the mass spectrometer's total ionization trace with the gas chromatograph's flame ionization trace.

To assist in identifying the alkaloids giving rise to the gc peaks, known *Erythrina* alkaloids were isolated by classical means in our studies,[7] and these were treated separately to the trimsylation–gc–ms technique to obtain their retention times and mass spectral parameters. In the present investigation, new *Erythrina* alkaloids were first pinpointed from their gc–ms data and tentative structures were assigned. The alkaloids were then isolated and further characterized. The isolated alkaloids' mass spectra were also obtained by the direct probe technique as the free alkaloids and by gc–ms as their TMS derivatives. Relative gc retention times and important mass spectral peaks for the trimsylated alkaloids are found in Table I.

The fact that some alkaloid derivatives have the same retention time has not been a serious problem, since no more than six to eight alkaloids are usually present in any one species.[7] Moreover, when two alkaloids with the same retention time have been found to occur in a species, it has been possible to identify them both from the mass spectrum of the gc peak containing them.

In assigning structures to the alkaloids encountered it

(7) D. S. Millington, D. H. Steinman, R. D. Johnson, C. A. Young, L. F. Becker, M. H. Mondal, R. T. Hargreaves, and K. L. Rinehart, Jr., papers in preparation.

(8) W. V. Ligon, Jr., J. C. Cook, Jr., and K. L. Rinehart, Jr., to be submitted.

(9) (a) K. Folkers and F. Koniuszy, *J. Amer. Chem. Soc.*, **62**, 436 (1940); (b) K. Folkers and J. Shavel, Jr., *ibid.*, **64**, 1892 (1942).

(10) Melting points were recorded on a Kofler apparatus and are uncorrected. Nmr spectra were taken in deuteriochloroform solutions at 100 MHz, unless stated otherwise. Gas chromatograms were obtained on a Varian Aerograph gas chromatograph, Model 1740, equipped with a flame ionization detector and a 0.25 in. (2-mm i.d.) × 6 ft glass column [packed with 3% OV-17 on Gas Chrom Q (Applied Science Laboratories, Inc.)] which allowed on-column injection. The gas chromatographic conditions used are summarized as follows: oven, temperature programmed from 225 to 250°; injector, 300°; detector, 300°; carrier gas, helium; flow rate, 30 ml/min; chart speed, 0.5 in./min. Gc–ms data were obtained using a Varian-MAT CH-7 mass spectrometer coupled *via* a commercial two-stage Watson–Biemann separator to a Varian 1740 gas chromatograph operated under conditions described

previously. The arrival of individual components in the ion source of the mass spectrometer was determined using a total ionization monitor connected to a strip chart recorder. The trace generated in this manner showed a component pattern identical with that obtained using the flame ionization detector. The mass spectrum of each component was determined at its total ion current maximum and recorded on magnetic tape. The data reduction system described elsewhere[10b] was applied to the spectra to produce bar graphs and tabular mass lists (both corrected for background and total ion current variations). Direct probe mass spectra were recorded on an Atlas MAT CH-4 or a Varian MAT CH-5 instrument; peak matching was carried out on a Varian MAT SM1B double focussing spectrometer. All mass spectra were determined at 70 eV. Thin-layer chromatography was carried out on silica gel GF-254 (E. Merck AG) employing chloroform–methanol (4:1 except as noted) as developing solvent and chloroplatinate spray to locate the alkaloids. Column chromatography employed neutral silica gel (E. Merck AG, less than 0.08 mm) or neutral alumina (Brinkmann, Grade II) with chloroform–methanol as eluting solvent. Mass spectra, nmr spectra, and microanalyses were obtained, respectively, by Mr. J. Carter Cook, Jr., Mr. Robert L. Thrift, and Mr. Josef Nemeth and their associates. (b) K.-E. Habfast, K. L. Rinehart, Jr., and J. Carter Cook, Jr., in "Biochemical Applications of Mass Spectrometry," G. A. Waller, Ed., Wiley, New York, N. Y., 1972, pp 121–132.

was convenient to decide first whether an alkaloid contained any hydroxyl groups. Each trimsyl derivative is characterized by the presence of an intense ion at m/e 73 [$(CH_3)_3Si^+$] in its mass spectrum and is thus easily distinguished in gc–ms studies from those alkaloids which do not form trimsyl derivatives, such as erysotrine (9) and erythraline (10). Two other alkaloids lacking hydroxyl groups—α- and β-erythroidine (1 and 2)—also appear underivatized (no m/e 73 ion) in gc peaks. These compounds will be discussed separately below.

The carbon skeletons of the known *Erythrina* alkaloids can be divided into two distinct groups—a small group, thus far only α- and β-erythroidine (1 and 2, respectively), which lack an aromatic ring but contain a lactone ring, and a larger group containing an aromatic ring. The aromatic alkaloids can be further divided into two subgroups, one characterized by the presence of a $\Delta^{2(1),6(7)}$-diene system, as in compounds 3–10, and the other by a $\Delta^{1(6)}$ olefinic linkage, as in compounds 11–19. For purposes of mass spectral assignment of the alkaloids' structures the latter difference is very important, since mass spectra of the two subgroups indicate that fragmentation is triggered in ring A and is independent of the substituents in ring D.[5] These spectral differences allow one to distinguish compounds which differ in ring A, but isomeric pairs such as erysodine (6) and erysovine (7), which differ only in the relative positions of substituents in ring D, cannot be distinguished by mass spectrometry alone.

The trimsyl (TMS) derivatives of the hydroxylic alkaloids measured in the present study (summarized in Table I) fragment in much the same way as the parent compounds.[5] The mass spectra of those alkaloids containing an isolated alkene unit (11–15) are dominated by ions resulting from the retro-Diels–Alder reaction (Figure 2, pathway a) and the fragment arising from elision of C-2 and C-3 and their substituents (pathway b). The loss of C_3H_6O (58 amu, pathway a) assigns a methoxyl group at C-3, while the substituent X at C-2 is defined by the ion $(M - C_3H_5OX)$ arising from path b. These are illustrated by the mass spectra of trimsyl-erythratidine (13-TMS) and trimsylerysotinine (11-TMS) in Figure 3. Alkaloids containing an alkenone unit (16–19) fragment by pathway a (but not pathway b) and also have fragmentations, shown in Figure 2, characteristic of the keto groups.[5] Illustrations are found in the spectra of erysotinone and erysoflorinone trimsyl derivatives (17-TMS and 16-TMS, respectively).

Since those alkaloids containing the conjugated diene system cannot undergo the retro-Diels–Alder reaction, and the alternative loss of C-3 and C-4 is not favored, the prominent fragmentation pathway of 3–8 and their trimsyl derivatives involves the simple loss of the allylic substituent at C-3 (not shown in Figure 2). This fragmentation allows facile distinction of the trimsyl derivatives of isomers 5 (and 4) from 3 (Table I and Figure 4), since the former gives a prominent ion from loss of a trimsyloxy group $(M - 89)^+$ while the latter gives an important ion from loss of a methoxy group $(M - 31)^+$. The same relationship holds for the mass spectra of the trimsyl derivatives of isomers 8 (M − TMSO) and 6 (or 7, M − CH₃O); see Table I and Figure 4.

The nonaromatic alkaloids α- and β-erythroidine (1 and 2) belong to the diene group and fragment by loss of the methoxyl substituent at C-3. Although it does not

Table I. Gas Chromatographic Behavior and Prominent Mass Spectral Peaks for Trimsyl Derivatives of *Erythrina* Alkaloids

Alkaloid derivative[a]	Rel retention time[g] [b]	M·+	(M − CH₃)+	(M − CH₃O)+ [j]	(M − TMSO)+ [j]	a·+ [j]	a − CO − H[j]	a − CO − H	a − CO − CH₄ / C₂H₄ − H	b·+ [j]	c	d	Others
2-TMS[b]	0.43	345 ( )		314 (12)									
5-(TMS)₂	0.95	429 (30)			340 (33), 338 (44), 313 (21), 337 (27)								
4-(TMS)₂[c]	0.89		414 (10)	398 (31), 396 (26), 395 (14)									
3-(TMS)₂	0.95	429 (9)	356 (22)										
8-TMS	1.07	371 (69)				371 (6), 282 (55), 280 (82), 255 (38), 279 (54)							264 (57), 236 (26), 235 (27), 310 (27)
6-TMS	1.00	371 (32)	356 (40)	340 (100), 338 (65), 337 (31)									
7-TMS[d]	1.07												
15-TMS	0.93	373 (3)		342 (13)		315 (100),[k] 314 (95)	300 (11)			315 (100),[k] 314 (95)			210 (19)
11-(TMS)₂	1.18	461 (1)	446 (8)			403 (100), 402 (40)	300 (11)			315 (36), 314 (23)			
12-(TMS)₂[c]	1.25												
13-TMS	1.34	403 (1)	388 (7)			345 (100), 344 (29)	242 (12)			257 (39), 256 (26)			
16-(TMS)₂	1.58	[445][k]	430 (9)	414 (4)		387 (26), 386 (9)	358 (37)				402 (21)	270 (100)	300 (14), 298 (14)
17-TMS	1.66	387 (1)	372 (7)	356 (7)		329 (58), 328 (11)	302 (23), 301 (75), 273 (20), 272 (19)	300 (100), 299 (19), 298 (17)			344 (29)	270 (43)	286 (14), 243 (16)
18-TMS[f]	1.47												

[a] For structures and names, see Figure 1. [b] Base peak = m/e 130. [c] Mass spectrum identical with that of 5-(TMS)₂. [d] Mass spectrum identical with that of 6-(TMS)₂. [e] Mass spectrum identical with that of 11-(TMS)₂. [f] Mass spectrum identical with that of 17-TMS. [g] Relative to 6-TMS = 1.00. [h] The relative gc retention times of free alkaloids are: β-erythroidine (2), 1.39; erysotrine (9), 1.17; erythraline (10), 1.21. [i] Molecular ion missing. [j] Of multiple ions peak in italics corresponds to column heading. Peaks predominantly due to isotope ions are omitted. [k] Fragmentation a gives the same values as b.
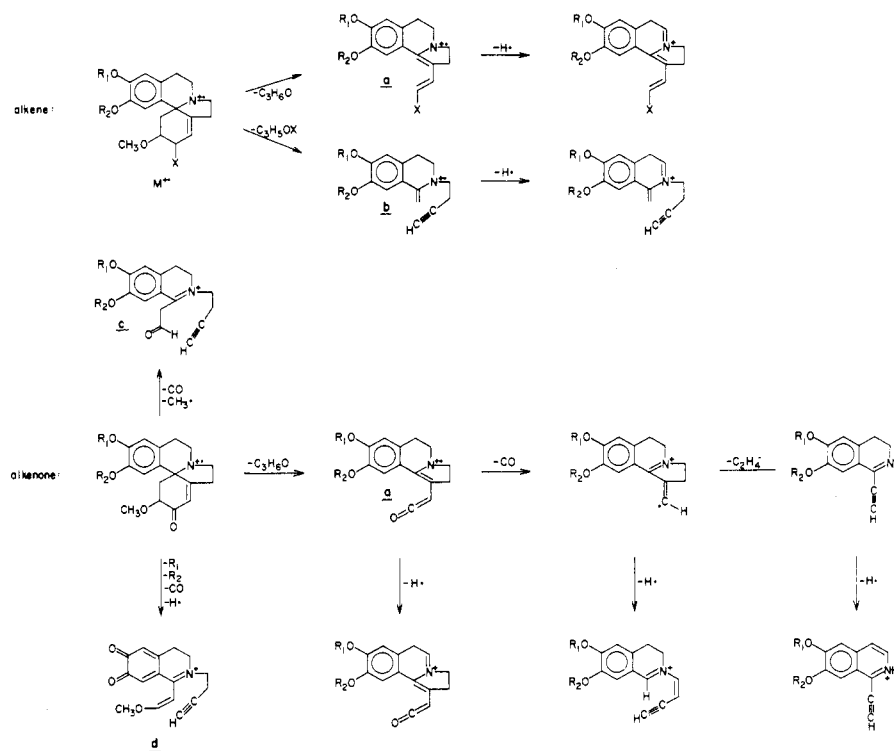
Figure 2. Principal mass spectral fragmentation pathways of *Erythrina* alkaloids.

contain a hydroxyl group, β-erythroidine is slowly converted into a monotrimsyl derivative (M·+ m/e 345, Table I), presumably *via* the enol form of the lactone, under the silylating conditions employed [N,O-bis(trimethylsilyl)acetamide, 30°], while its α isomer (the corresponding unsaturated conjugated lactone) is not. Since α- and β-erythroidine are not resolved on the gc column, this affords a rough estimate of the amount of each isomer present in a mixture.

Erythrina folkersii **Krukoff and Moldenke.** The gas chromatogram of the "free" alkaloids[2] of *E. folkersii* after trimsylation, reproduced in Figure 5, shows two strong peaks, B and D, and two weak peaks, A and C, followed by a trace component. The structures assigned to the alkaloids producing the gc peaks were deduced from their mass spectra and gc retention times after comparison with available standards.

The trace component was identified as erysotrine (9) by comparison of gc retention time and mass spectrum with those of an authentic sample isolated in our laboratory from another *Erythrina* species (see Experimental Section) and identified by uv, nmr, and mass spectrometry.[7] Peak C in Figure 5 was identified as that for trimsylerysodine (6-TMS) by comparison of the retention time and mass spectrum of a sample of 6-TMS prepared from an authentic sample of erysodine isolated from *E. macrophylla* Alph. DeCandolle and identified by melting point and nmr and mass spectra.[7]

Peak C contained two trimsyl derivatives. Mass spectra recorded for the leading edge of peak D during the gc–ms run shown in Figure 5 indicated it to contain trimsylerysovine (7-TMS), whose major mass spectral ions and retention time were identical with those of a sample of 7-TMS prepared from an authentic sample of erysovine isolated in our laboratory from *E. guatemalensis* Krukoff and identified by melting point and nmr and mass spectra.[7]

Components A and B gave identical mass spectra, with molecular ions at m/e 429 indicative of ditrimsyl derivatives of alkaloids with the formula $C_{17}H_{19}NO_3$, and with strong peaks at m/e 340 (M − TMSO)+ characteristic of an *Erythrina* alkaloid containing a conjugated diene system and a hydroxyl group at C-3. On this basis the alkaloids must have been 5 (a new alkaloid) and 4 (erysonine), rather than the isomeric 3 (erysopine). To confirm this conclusion, authentic ditrimsylerysopine [3-(TMS)₂] was prepared from a sample of erysopine, isolated from seeds of *E. macrophylla* Alph. DeCandolle and identified by melting point and nmr and mass spectra;[7] it gave the expected strong peak at M − CH₃O rather than M − TMSO although it had the same retention time as component B (Table I). To decide which peak (A or B) arises from 5 and which from 4, standard samples of the parent alkaloids which would correspond to 5 and 4 were obtained by demethylation[11] of the known alkaloids 6 (erysodine) and 7 (erysovine), respectively (Figure 6). Demethylerysodine, the known alkaloid erysonine (4),[12] was shown to produce peak A, while demethylerysovine (5) produces peak B. We have assigned the name erysoline to the new alkaloid 5 and have isolated it by column chromatography of the "free" alkaloid extracts of *E. folkersii*. Erysoline was shown to be identical by tlc, uv, nmr, gc, and mass spectrometry with a standard sample of demethylerysovine. Mass spectral data for erysoline (5) are given in Table II, those for its trimsyl derivative in Table I and Figure 4.

A mass spectrum from the trailing edge of peak D indicated it to arise from the trimsyl derivative of an isomer of the known alkaloids 6 (erysodine) and 7

(11) V. Prelog, A. Langermann, O. Rodig, and M. Terubah, *Helv. Chim. Acta*, **42**, 1301 (1959).
(12) K. Folkers, J. Shavel, Jr., and F. Koniuszy, *J. Amer. Chem. Soc.*, **63**, 1544 (1941).
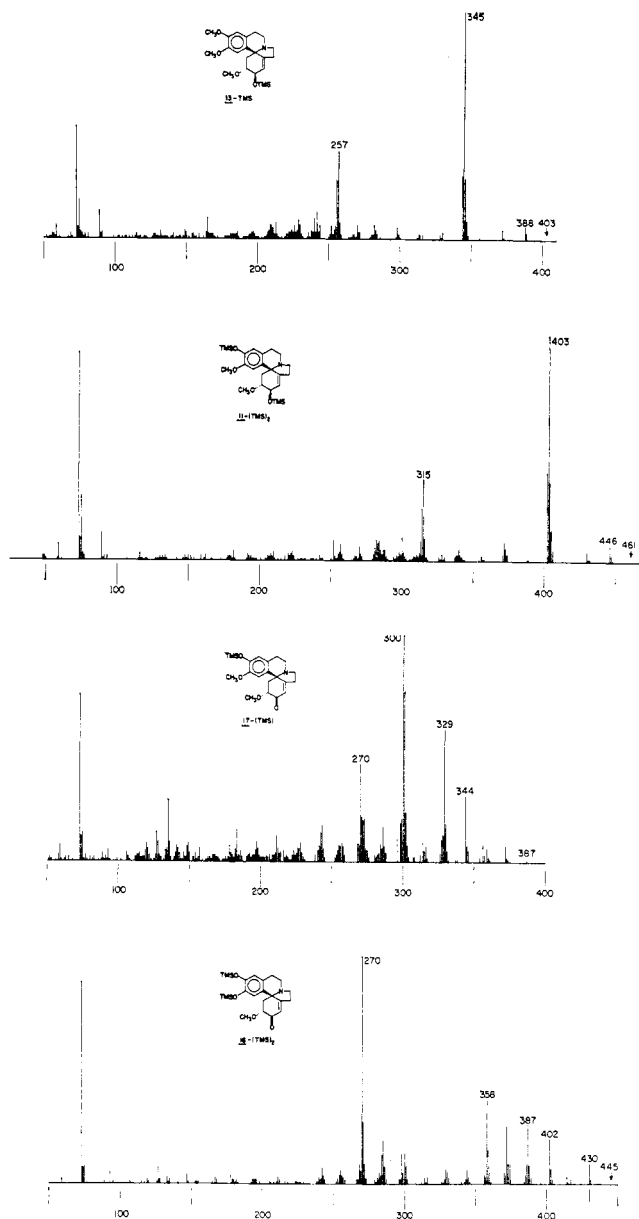
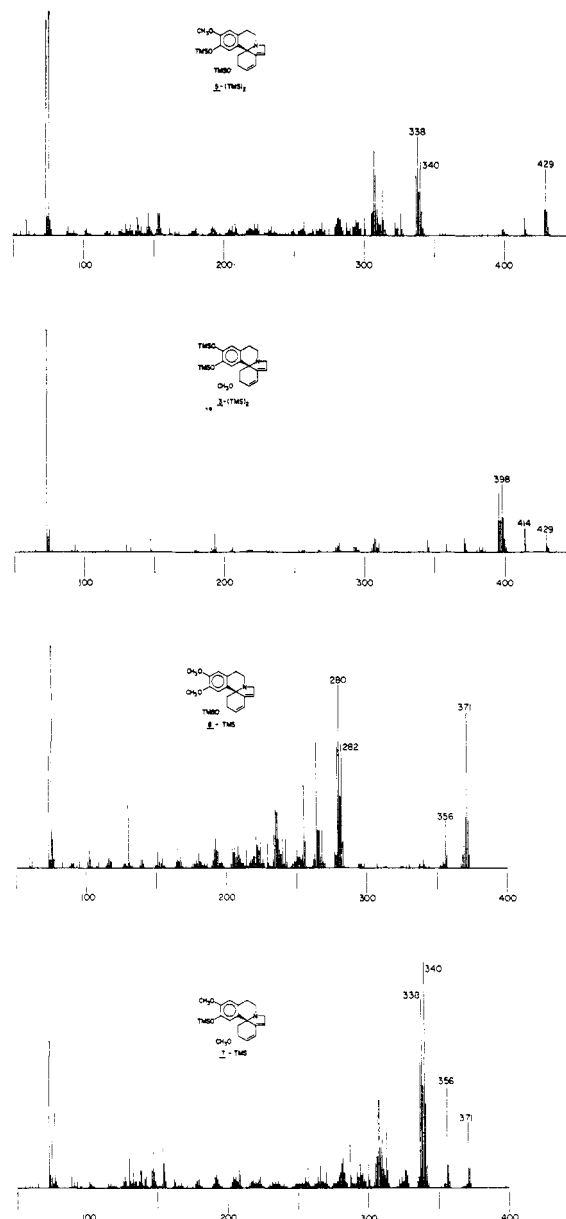**Figure 3.** Mass spectra of the trimsyl derivatives of **13, 11, 17,** and **16.**

Figure 4. Mass spectra of the trimsyl derivatives of isomers **5** and **3** and isomers **8** and **7.**

(erysovine); it appeared to have the structure **8-TMS**, as deduced from its fragmentation pattern (Table I and Figure 4). Thus, the spectrum indicated a monotrimsyl derivative (M·+ 371) of a diene with a hydroxyl group at C-3 (strong M − TMSO peak at m/e 282). The alkaloid giving rise to the latter part of peak D is new and has been named erythravine (**8**). Erythravine was also isolated by column chromatography of the "free" alkaloids of *E. folkersii* but has not been induced to crystallize in spite of numerous attempts. Its uv maxima at 225 nm (ϵ 14,000) and 282 (3070) are consistent with those of an *Erythrina* alkaloid possessing a $\Delta^{2(1),6(7)}$-diene system,[2b] while signals in the nmr spectrum (Table III) corresponding to two phenolic methyl ethers and its mass spectra (Tables I and II, Figure 4) are in accord with the structure **8** assigned to erythravine.

The "liberated" alkaloids[2] from *E. folkersii* consisted mainly of erysodine (**6**) and erysovine (**7**), with smaller amounts of erysopine (**3**) and erysonine (**4**), all
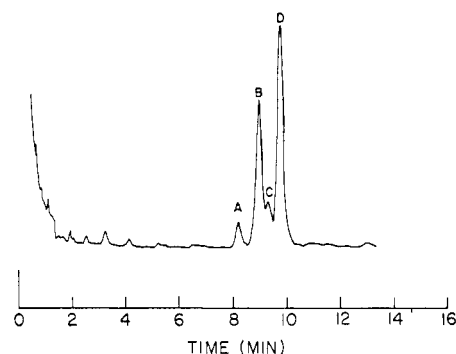

Figure 5. Gas chromatogram of trimsyl derivatives of the "free" alkaloids of *E. folkersii.*

identified by comparison of gc–ms behavior (as trimsyl derivatives) to authentic samples (see above). In summary, the present study has identified the following alkaloids in *Erythrina folkersii*: erysotrine, erysonine,

Table II. Prominent Mass Spectral Peaks for New *Erythrina* Alkaloids from *E. folkersii* and *E. salviiflora*

Alkaloid	M	M − OH	M − CH$_3$O	a	a − CO	b	c
5[a]	285 (100)	268 (89), 266 (21)	254 (22)				
8	299 (94)	*282 (100)*, 280 (17)	266 (23)[b]				
13	331 (10)		300 (12)	*273 (81)*, 272 (18)		*257 (100)*, 256 (20)	
11[a]	317 (8)		286 (14)	*259 (93)*, 258 (23)		*243 (100)*, 242 (26)	
17[a]	315 (3)			*257 (75)*, 256 (11)	229 (70), *228 (100)*	242 (15)[c]	272 (25)

[a] The spectra of **5** and **4**, of **11** and **12**, and of **17** and **18** are identical. [b] M − CH$_3$O − H$_2$. [c] b − H.

Table III. Nmr Peaks of Alkaloids Isolated

Alkaloid	H-14	H-17	H-2	H-1	H-7	H-3	15-OCH$_3$	16-OCH$_3$	3-OCH$_3$	−CH$_2$−[b]
Erythravine (8)[c]	6.88 s	6.68 s	6.57 q (10,2)	6.05 d (10)	5.77 s b	4.53 m	3.90 s	3.80 s		3.75–1.75 c
Erysoline (5)[d]	6.69 s	6.46 s	6.34 m	5.78 m	5.56 m	4.20 m		3.79 s		3.70–1.55 c
Erythratidine (13)[c]	6.70 s	6.59 s	4.56 m	5.93 m	e	3.70 m	3.94 s	3.89 s	3.44 s	3.80–1.80 c[e]
Erysotinone (17)[c]	6.80 s	6.58 s		6.18 m	e	4.10 q	3.84 s		3.56 s	3.50–2.08 c[e]
lit.[6] values	6.77 s	6.55 s		6.12 s	e	4.07 q (J_{AX} + J_{BX} = 19)	3.80 s		3.51 s	f
Erysotine (11)[d]	6.68 s	6.48 s	4.45 m	5.87 m	e	3.6 m	3.80 s		3.36 s	3.30–1.80 c[c]
Erysosalvine (12)[d]	6.60 s	6.55 s	4.45 m	5.87 m	e	3.6 m		3.86 s	3.36 s	3.30–1.75 c[e]
Dihydroerysodine (15)[c]	6.73 s	6.65 s	g	5.67 m	e	3.60 m	3.89 s		3.34 s	3.30–1.50 c[e,g]

[a] s = singlet, d = doublet, q = quartet, m = multiplet, c = complex. [b] H-4, H-8, H-10, and H-11. [c] 100 MHz. [d] 60 MHz. [e] 7-CH$_2$ included in complex. [f] Not reported. [g] 2-CH$_2$ included in complex.
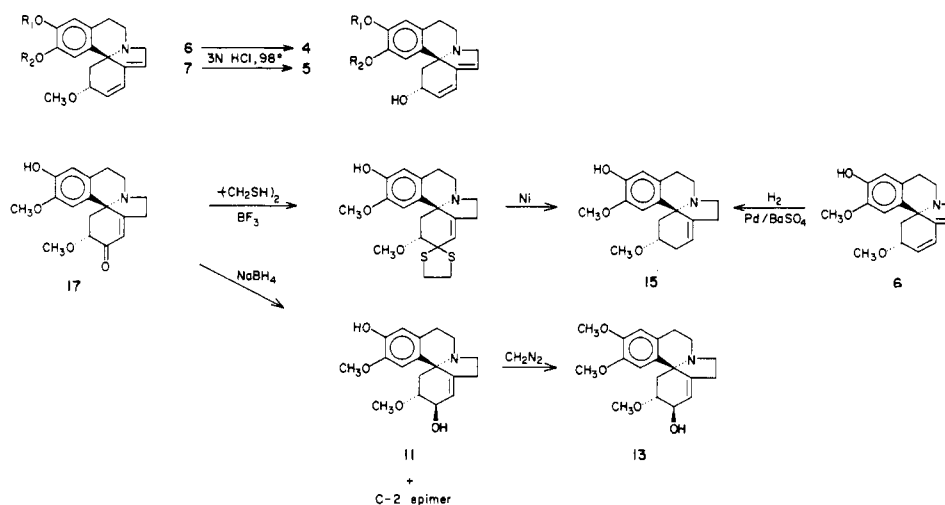
Figure 6. Interconversions of *Erythrina* alkaloids.

erysodine, erysovine, erysopine, erysoline, and erythravine, the last two new alkaloids. The new alkaloid erythravine is also one of the major alkaloids found in seeds of *E. steyermarkii* Krukoff and Barneby.[7] It is of chemotaxonomic interest that all of these alkaloids contain the diene nucleus (4–9). An earlier study reported erysodine and erysovine in *E. folkersii*, in agreement with the present results, but did not identify erysotrine, erysonine, erysopine, erysoline, or erythravine.[9] On the other hand, those studies[9] indicated erythraline (10) to be present, an alkaloid we do not find in *E. folkersii*, although we have identified it in *E. macrophylla* Alph. DeCandolle and other species.[7]

Erythrina salviiflora **Krukoff and Barneby.** A more complex mixture, including several new alkaloids, was indicated by the gc traces of the "free" and "liberated" bases[2] extracted from *E. salviiflora* as shown in Figure 7. While the minor components A, B, and C were recog-

nized from their mass spectra and gc retention times as corresponding to the trimsyl derivatives of the known alkaloids erysopine (3), erysodine (6), and erysovine (7), respectively, already discussed above under *E. folkersii*, peaks D–J corresponded to previously unknown alkaloids. Tentative structures were initially assigned to the four major components D, E, I, and J (trimsyl derivatives of **11, 12, 17,** and **13,** respectively) from their mass spectra (Table I) and these were confirmed by isolating by column chromatography the alkaloids (**11, 12, 17,** and **13**) giving rising to peaks D, E, I, and J and correlating them chemically with known compounds.

Three of the major components (D, E, and J) have similar fragmentations (Table I and **17**-TMS in Figure 3) which correspond to that for the alkene substitution pattern in ring A shown in Figure 2. The prominent peaks (Table I: a = M − C$_3$H$_6$O; b = M − C$_3$H$_5$-
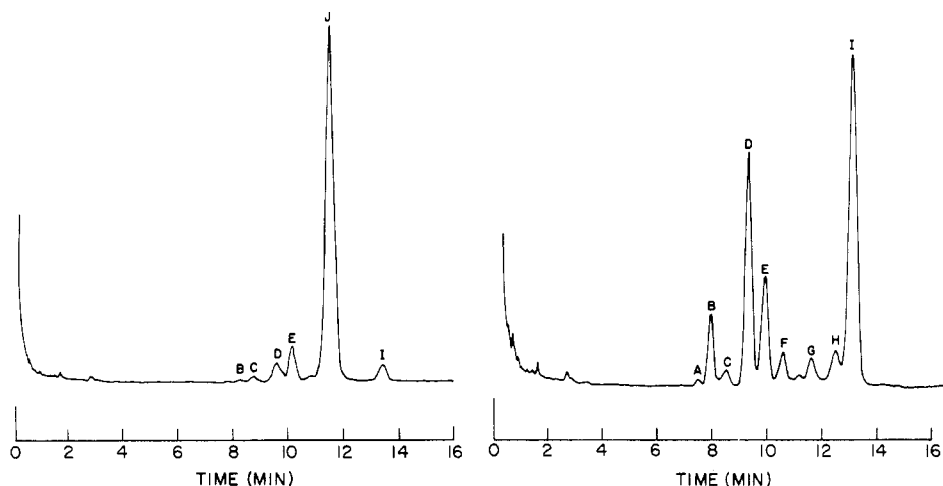
Figure 7. Gas chromatogram of trimsyl derivatives of the "free" (left) and "liberated" (right) alkaloids of *E. salviiflora*.

OTMSO) for D, E, and J are those of an *Erythrina* alkaloid containing one double bond in ring A, a methoxy group at C-3, and a trimsyloxy group at C-2. The first two are isomers, each having one methoxy and one trimsyloxy substituent in ring D, while, from the difference in molecular weights of 58 (89 − 31) amu for components D and E vs. component J, component J must have two methoxy groups in ring D. This assigns the alkaloid giving rise to component J the structure **13**. Although one cannot locate the aromatic methoxy and trimsyloxy groups from the mass spectra of D and E, this was effected by correlation with the alkaloid (**17**) giving rise to component I, as discussed below.

Component I showed a mass spectral fragmentation pattern (Table I and **17**-TMS in Figure 3) similar to that reported for erythratinone (**19**),[5] and its molecular weight indicates it to be derived from **17** (Figure 1) or the isomeric alkaloid in which the ring D substituents are interchanged. Among the alkaloids isolated by column chromatography the ketonic alkaloid (**17**) giving rise to component I was readily identified by its ir and uv spectra and its trimsyl derivative was shown to give the gc peak I. The alkaloid **17** was converted by ethanedithiol to its thioketal (Figure 6), which was reduced by Raney nickel to the known alkaloid dihydroerysodine (**15**).[13] An authentic sample of **15**, prepared by catalytic hydrogenation of erysodine (**6**), was identical with the material derived from the ketone **17** in tlc and gc–ms behavior of its trimsyl derivative; a mixture melting point was undepressed. This assigns the ketonic alkaloid the structure **17**, which corresponds to the compound obtained as a racemic synthetic intermediate by Mondon and Ehrhardt[6a] and later called erysotinone by Barton, Boar, and Widdowson.[3b] This is the first reported isolation of natural (and optically active) erysotinone (**17**).

Sodium borohydride reduction of **17** (Figure 6) gave what was presumably an epimeric mixture of alcohols (previously prepared as a racemate[6a] and subsequently named erysotine)[3b] which could not be resolved by gc after trimsylation. However, the gc retention time of the trimsyl derivative was the same as that of component D in Figure 7 and different from that of component

E; the mass spectrum was the same as those of D and E. Since the position of the aromatic methoxyl group is known in **17** (from **15**) this result assigns the structure **11** to the isomer which gives rise to component D and, therefore, the structure **12** to the isomer which gives rise to component E. Barton, Boar, and Widdowson[3b] have given the name erysotine to the alcohol resulting from reduction of **17**;[6a] the present report describes the first isolation of natural (optically active) erysotine. We have given the name erysosalvine to the previously unreported alkaloid **12**. Alkaloids **11** and **12** were isolated as a mixture from column chromatography, but it was possible to crystallize **11** (the alkaloid giving rise to component D) from the mixture. The nmr spectrum of **11** compared favorably with that reported for erythratine (**14**)[3a] except that the methylenedioxy group of erythratine was replaced by an aromatic methoxy group and a phenolic hydroxyl group. Treatment of **11** with ethereal diazomethane gave **13** (erythratidine),[14] identical with the isolated alkaloid giving rise to peak J in Figure 7. It is of chemotaxonomic interest that all of the major alkaloids of *E. salviiflora* contain the isolated alkene skeleton (**11–13, 17**).

The minor alkaloids giving rise to components F, G, and H (Figure 7) were not isolated, but structural conclusions can be drawn from the mass spectra of the trimsyl derivatives. Component G gives a mass spectrum identical with that of component I, the trimsyl derivative of **17** (erysotinone), and the two are, therefore, isomers, with component G a derivative of **18** (which we propose to name erysosalvinone), where the aromatic methoxyl and hydroxyl groups of **17** are interchanged.

The mass spectrum of component H exhibited the same fragmentations shown by components G and I but with all the major peaks above m/e 300 shifted to higher masses by 58 amu (89 − 31, TMS − CH$_3$). The parent alkaloid then is assigned structure **16** (and named erysoflorinone) with two phenolic hydroxyl groups.

The mass spectrum of component F contained a weak molecular ion at m/e 459, but its most abundant fragment ions occur at the same masses with generally similar relative abundances as the trimsyl derivatives of **17** and **18**—m/e 329 (80), 314 (89), 300 (100), 270 (43).

(13) M. Tomita and H. Yamaguchi, *Pharm. Bull.*, **4**, 225 (1956).

(14) V. Deulofeu, *Chem. Ber.*, **85**, 620 (1952).

From the fragmentation pathways shown in Figure 2 this indicates like substituents on C-1 and on C-5–C-17, as well as oxygen on C-2. Two reasonable structural possibilities can be suggested for component F. The simplest is that it is a trimsyl derivative of the enol form of **17** or **18**, with the generalized formula **20**. However, pure erysotinone itself (**17**) does not show any tendency to enolize under the silylating conditions. An alternative, biosynthetically more exciting,[3] possibility is that component F arises from a dienol and has the generalized structure **21**. With appropriate hy-

20　　　　　21
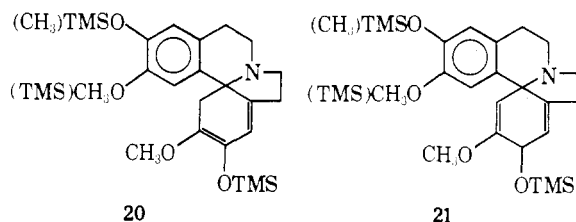
drogen transfers and trimsyl losses either structure could account for the prominent mass spectral peaks of F at m/e 403 (M − 56) and m/e 342 (corresponding to m/e 344 in the spectrum of **17**-TMS). Both possible structures are receiving the further study they warrant.

The success of the present investigation, which has increased the number of known *Erythrina* alkaloids by about 40%,[2,4] clearly indicates that combined gc–ms is the method of choice for the analysis of mixtures of *Erythrina* alkaloids. Several new alkaloids have been detected in other *Erythrina* species by gc–ms and studies designed to establish their identity will be reported separately.[7]

Experimental Section[10]

Spectra. Mass spectra of the new alkaloids and the gc–ms characteristics of their trimsyl derivatives are summarized in Tables II and I, respectively. Nmr spectral data are given in Table III.

Preparation of Trimsyl (Trimethylsilyl) Derivatives. A sample of an alkaloid or mixture of alkaloids (1–2 mg) was dissolved in 30 μl of acetonitrile, then 30 μl of N,O-bis(trimethylsilyl)acetamide was added and the solution was allowed to stand at 30° for at least 30 min in a screw-cap vial fitted with a Teflon liner. Samples were removed with a syringe through a septum in the cap. Only freshly prepared solutions were used for gc–ms.

Isolation of Alkaloids from Erythrina Seeds. About 200 g of ground seeds in a Soxhlet apparatus was defatted by extraction with hexane for 16 hr, then extracted with methanol for 36 hr. After the methanol had been removed *in vacuo*, the residue was dissolved in 0.1 N hydrochloric acid and the solution was extracted thoroughly with chloroform. The aqueous solution was made basic by addition of solid sodium bicarbonate and extracted again with chloroform. The latter extract was dried over magnesium sulfate and the solvent was evaporated to yield the "free" alkaloids. The remaining aqueous solution was adjusted to pH 1 by addition of concentrated hydrochloric acid, heated to 60–70° for 1–3 hr, then made basic again and extracted with chloroform. This extract was dried over magnesium sulfate and the solvent was evaporated to give the "liberated" alkaloids. The two alkaloid fractions were processed separately to identify and isolate their components.

Known Alkaloids Used as Standards. Crystalline samples of erysodine (**6**), mp 205–205.5° (lit.[2a] 204–205°), and erysopine (**3**), mp 230–235° (lit.[2a] 241–242°), were isolated from *E. macrophylla* Alph. De Candolle (*Krukoff 1969–167*, from Guatemala) in yields of 0.05 and 0.005%, respectively. The sample of erysovine (**7**) used in the investigation was isolated from *E. guatemalensis* Krukoff (*Krukoff 1969–246*, from Guatemala) in 0.06% yield, and had mp 178–179° (lit.[2a] 178–179.5). Noncrystalline samples of erysotrine (**9**) and erythroidine (α and β, **1** and **2**) were isolated from a not yet identified *Erythrina* species (*Krukoff 1969–104*, from Costa Rica) and *E. berteroana* Urban (*Krukoff 1967–3*, from Guatemala), respectively, while erysonine (**4**) was prepared by demethylation of

erysodine (**6**) (*vide infra*). The alkaloids were fully characterized by comparison of their uv, ir, nmr, and mass spectra with those cited in the literature. Complete reports of our studies[7] with the four species cited will be published subsequently.

Isolation of Erythravine (8) and Erysoline (5) from the "Free" Alkaloids of *E. folkersii* Krukoff and Moldenke. Chromatography of the "free" alkaloids (470 mg, 0.24%) from 200 g of *E. folkersii* seeds (*Krukoff 1969–239*, from Guatemala) on a column of silica gel, eluting with chloroform–methanol (99:1), gave first 12 mg of erysotrine (**9**), then 50 mg of a mixture of erysodine (**6**) and erysovine (**7**), then 150 mg of a fraction containing the new alkaloid erythravine (**8**). The last fraction was rechromatographed on alumina, using chloroform–methanol (99:1), to give **8** as a faintly yellow oil (95 mg), which could not be induced to crystallize but was homogeneous on tlc and gc (after trimsylation); uv (absolute EtOH) 225 nm (ϵ 14,400) and 282 (3070).

Anal. Calcd for $C_{18}H_{21}NO_3$: mol wt, 299.1521. Found: mol wt, 299.1520 (HRMS).

Further elution of the column with chloroform–methanol (97:3) afforded another fraction (95 mg), containing mostly the new alkaloid erysoline (**5**). Recrystallization of the fraction from ether gave erysoline (**5**, 11 mg), melting point broad. This material was pure by tlc and gave a single peak on gc after trimsylation; uv (absolute EtOH) 225 nm (ϵ 11,900) and 285 (2950).

Anal. Calcd for $C_{17}H_{19}NO_3$: mol wt, 285.1365. Found: mol wt, 285.1362 (HRMS).

The "liberated" alkaloids (0.560 g, 0.28%) were chromatographed over silica gel employing chloroform–methanol (99:1) to give two fractions, the first containing erysodine (**6**) and erysovine (**7**), the second containing erysopine (**3**) and erysonine (**4**); all were identified by gc–ms.

In three other extractions of seeds of *E. folkersii* (*Krukoff, 1969–239*), the yields of "free" alkaloids were 0.17, 0.24, and 0.82%, and the yields of "liberated" alkaloids were 0.11, 0.01, and 0.13%.

Demethylation of Erysovine (7) to Give Erysoline (5). Erysovine (**7**, 83 mg) was heated at 98° for 2 hr with 2 ml of 3 N hydrochloric acid, then the solution was made basic using saturated sodium bicarbonate solution and extracted repeatedly with chloroform. The combined extracts were dried over magnesium sulfate, filtered, and evaporated to leave 68 mg of a gum which was purified by preparative tlc over silica gel. The demethylerysovine isolated (33 mg) had uv, nmr, and mass spectra identical with those of erysoline (**5**), isolated in the preceding section. Demethylerysovine (**5**) also had the same gc retention time as erysoline after trimsylation, while the isomeric authentic erysonine (**4**) was eluted with a shorter retention time.

Isolation of Erythratidine (13) from the "Free" Alkaloids of *E. salviiflora* Krukoff and Barneby. The "free" alkaloids (272 mg, 0.14%) extracted from 200 g of seeds of *E. salviiflora* (*Krukoff 1969–58*, from Guatemala)[15] consisted mostly of erythratidine (**13**), which was purified by column chromatography on alumina, eluting with chloroform–methanol (98:2) to give 200 mg of **13** followed by 12.5 mg of a mixture of erysotine and erysosalvine (**11** and **12**, respectively; see below). Three crystallizations of **13** from ether–petroleum ether gave pure erythratidine (**13**): mp 119–120°; $[\alpha]^{25}\text{D}$ +273° (c 0.3, absolute EtOH); uv max (absolute EtOH) 232 nm (ϵ 7820) and 287 (3550) [lit.[14] mp 120–121°, $[\alpha]\text{D}$ +279° (EtOH)].

Anal. Calcd for $C_{19}H_{25}NO_4$: mol wt, 331.1783. Found: mol wt, 331.1770 (HRMS).

Isolation of Erysotinone (17), Erysotine (11), and Erysosalvine (12) from the "Liberated" Alkaloids of *E. salviiflora* Krukoff and Barneby. The "liberated" alkaloids (1.181 g, 0.59%) from 200 g of seeds of *E. salviiflora* (*Krukoff 1969–58*)[15] were chromatographed on silica gel, eluting with chloroform–methanol (98:2). The first component to be eluted was crude erysotinone (**17**, 0.38 g), which was further purified by chromatography on an alumina column, employing chloroform–methanol (4:1). Two recrystallizations from ether gave 148 mg of **17** as colorless needles: mp 177–179°; $[\alpha]^{25}\text{D}$ +342° (c 0.28, absolute EtOH); uv max (absolute EtOH) 226 nm (ϵ 17,600); ir (CHCl₃) 1675 cm⁻¹ (C=O) [lit.[6] mp 196–197° (racemic); uv max 228 nm (log ϵ 4.5); ir (KBr) 1680 cm⁻¹ (C=O)].

Anal. Calcd for $C_{18}H_{21}NO_4$: C, 68.57; H, 6.67; N, 4.44; mol

(15) Krukoff and Barneby (personal communication) have recently split "*E. mexicana*" into two species (*E. salviiflora* Krukoff and Barneby and *E. mexicana* Krukoff). The seeds employed in the present investigation were originally identified as *E. mexicana* [B. A. Krukoff, *Mem. N. Y. Bot. Gardens*, **20**, 159 (1970)] but have subsequently been classified as *E. salviiflora*.

wt, 315.1440. Found: C, 68.45; H, 6.88; N, 4.43; mol wt, 315.1467 (HRMS).

Continuation of the chromatography of the "liberated" alkaloids from E. salviiflora eluted a small amount of erysodine (6) and erysovine (7), mainly the former, then 0.44 g of a mixture of erysotine (11) and erysosalvine (12) which could not be resolved by chromatography on either silica gel or alumina columns. Extraction of the purified mixture (0.17 g) with boiling ether left 42 mg of an insoluble residue which, after two recrystallization from chloroform–ether, gave 18 mg of pure erysotine (11) as colorless crystals, mp 225–227°.

Anal. Calcd for $C_{18}H_{23}NO_4$: mol wt, 317.1628. Found: mol wt, 317.1630 (HRMS).

Erysosalvine (12) was not obtained pure, the best sample being contaminated with about 20% of erysotine as shown by gc. Its mass spectrum showed a molecular ion at m/e 317, and was identical with that of pure erysotine (Table II).

Reduction of Erysotinone with Sodium Borohydride.[6a] Erysotinone (17, 100 mg) was warmed at 65° with 150 mg of sodium borohydride in 3 ml of methanol until tlc indicated complete reaction after about 30 min. The solution was then diluted with 30 ml of water, heated to 100°, cooled, and extracted repeatedly with chloroform. The combined extracts were dried over magnesium sulfate, filtered, and evaporated to yield 65 mg of erysotine (11), presumably mixed with its C-2 epimer. No further purification could be achieved by chromatography on silica gel or alumina. Gas chromatography of the trimsyl derivative gave a single peak, coincident in retention time with ditrimsylerysotine [11-(TMS)₂].

Preparation of Dihydroerysodine (15). A. From Erysodine (6).[11] Erysodine (6, 60 mg) was hydrogenated for 2 hr over 25 mg of 5% palladium–barium sulfate catalyst in 12 ml of ethanol. The solution was filtered through Celite, solvent was removed, and the residue was chromatographed on silica gel, eluting with chloroform–methanol (98:2) to afford 40 mg (60%) of pure dihydroerysodine (15), mp 208–209° (lit.[6] 212°).

Anal. Calcd for $C_{18}H_{23}NO_3$: mol wt, 301.1678. Found: mol wt, 301.1692 (HRMS).

B. From Erysotinone (17). Erysotinone (17, 60 mg) was dissolved in 0.15 ml of ethanedithiol, and 0.1 ml of boron trifluoride etherate was added. After standing 14 hr at 20° the solution was diluted with ether and the resulting precipitate was washed with dry ether. The oily residue (45 mg) was homogeneous on tlc (CHCl₃–MeOH, 9:1): ir 1517 cm⁻¹ (but no absorption at 1675 cm⁻¹); nmr (60 MHz) δ 6.73, 6.51 (s, 1, aromatic H), 6.11 (m, 1, H-1), 3.84 (s, 3, 15-OCH₃), 3.56 (s, 3, 3-OCH₃) ppm. Without further purification, the thioketal derivative was heated for 0.5 hr with 1.5 g of Raney nickel (W-2) in 10 ml of refluxing ethanol. The solution was then filtered through Celite, concentrated, and chromatographed on a silica gel preparative tlc plate to give 6 mg of dihydroerysodine (15), mp 204–206°, whose ir and mass spectra, tlc behavior (CHCl₃–MeOH:9:1), and gc retention time (as its trimsyl derivative) were identical with those of the authentic sample of dihydroerysodine (15) prepared in part A.

Conversion of Erysotine (11) and Erysosalvine (12) into Erytratidine (13). A mixture of erysotine (11) and erysosalvine (12) (4:1, 15 mg) was dissolved in methanol (0.1 ml) and excess ethereal diazomethane was added to the solution, which was allowed to stand until tlc indicated complete reaction. The product was recrystallized from ether to give erythratidine (13, 5 mg), with melting point, tlc behavior, and gc retention time (after trimsylation) identical with those of authentic erythratidine described above.

Identification of Erythrina Seeds. The seeds used in these studies were collected and identified by B. A. Krukoff, Consulting Botanist of Merck Research Laboratories and Honorary Curator of New York Botanical Garden. They are as follows: *Krukoff 1969–239* identified as *Erythrina folkersii* Krukoff and Moldenke; *Krukoff 1969–58*, as *E. salviiflora* Krukoff and Barneby; *Krukoff 1969–167* as *E. macrophylla* Alph. De Candolle; *Krukoff 1969–246* as *E. guatemalensis* Krukoff; *Krukoff 1967–3* as *E. berteroana* Urban; *Krukoff 1969–145* as *E. steyermarkii* Krukoff and Barneby; and *Krukoff 1969–104* (a not yet identified Erythrina species).

All samples of seeds are authentic, that is, backed by herbarium material deposited at the New York Botanical Garden and other herbaria of the world.

Stereoselective Total Synthesis of (±)-Longipinenes

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Contribution from the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Sendai 980, Japan. Received September 11, 1973.

Abstract: A total synthesis of racemic α- and β-longipinenes (1a and 1b, respectively) is described. The key step is the photocyclization of a cyclodeca-1,5-diene derivative (5b) to a tricyclo[5.3.0.0²,⁸]decane structure (24). The photocyclization product was converted to longipinenes *via* Tiffeneau–Demjanov ring expansion of an amino alcohol (30a) derived therefrom.

The (+)-α isomer of longipinene has been isolated from the wood of *Pinus silvestris*,[1] Swedish sulfate turpentine,[2] and *P. longifolia*,[3] and the structure 1a has been assigned on the basis of spectral similarities with those of α-pinene and by chemical transformation, chiefly conversion into (+)-longibornyl chloride on the action of hydrogen chloride.[1,4] Recently, (−)-β-longipinene (enantiomer of 1b),[5] along with (−)-α

(1) L. Westrfelt, *Acta Chem. Scand.*, **17**, 2351 (1963); **20**, 2826 (1966).
(2) L. Westfelt, *Acta Chem. Scand.*, **20**, 2841 (1966).
(3) S. Dev, personal communication.
(4) L. Westfelt, *Acta Chem. Scand.*, **21**, 159 (1967).
(5) N. H. Andersen, personal communication.

isomer,[5,6] has been found in liverwort (*Scapania undulata*).

Longipinenes, as well as copaenes 2,[7] ylangenes 3,[8] and bergamotenes 4,[9] comprise a pinane moiety in the carbon framework as a conspicuous structural feature.

(6) A. Matsuo, M. Nakagawa, S. Sato, R. Utosei, and S. Hayashi, Annual Meeting of the Chemical Society of Japan, Tokyo, Apr 1973.
(7) (a) (α-Copaene) P. de Mayo, R. E. Williams, G. Büchi, and S. H. Feairheller, *Tetrahedron*, **21**, 619 (1965); V. H. Kapadia, B. A. Nagasampagi, V. G. Naik, and S. Dev, *ibid.*, **21**, 607 (1965); (b) (β-copaene) L. Westfelt, *Acta Chem. Scand.*, **21**, 152 (1967).
(8) (α-Ylangene) O. Motl, V. Herout, and F. Sorm, *Tetrahedron Lett.*, 451 (1965); (β-ylangene) see ref 7b.
(9) V. Herout, V. Ruzicka, M. Vrany, and F. Sorm, *Collect. Czech. Chem. Commun.*, **15**, 373 (1950). See also ref 10c.