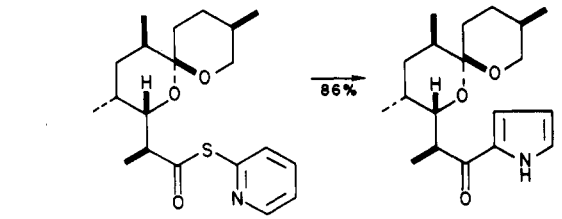

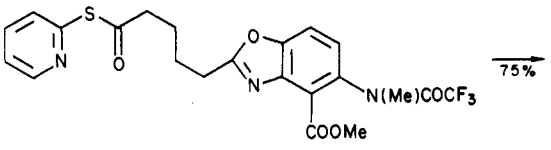

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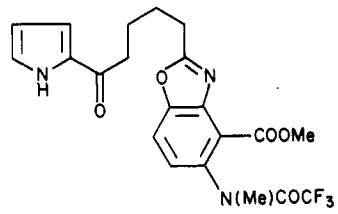

12

The ready availability of *N*-(*N*,*N*-dimethylamino)pyrrole (**2**) coupled with the extreme ease with which it undergoes lithiation, conversion into a Grignard reagent, and removal of the dimethylamino protecting group renders **2** an exceedingly useful reagent in organic synthesis.

Acknowledgment. This research was supported by a Public Health Service Research Grant from the National Institute of Allergy and Infectious Diseases (AI-17410). We are indebted to Dr. Heinz Gschwend for valuable discussions.

Registry No. **2**, 78307-76-3; **3**, 78307-77-4; **4**, 78307-78-5; **5**, 78307-79-6; **6**, 78328-70-8; **7**, 78307-80-9; **8**, 73252-31-0; **9**, 78307-81-0; **10**, 78307-82-1; **11**, 78307-83-2; **12**, 78328-71-9; 2,5-dimethoxytetrahydrofuran, 696-59-3; *unsym*-dimethylhydrazine, 57-14-7; heptanal, 111-71-7; 1-(dimethylamino)-2-heptanoylpyrrole, 78307-84-3; *S*-(2′-pyridyl) 2-cyclohexylpropanethioate, 78307-85-4; 1-(dimethylamino)-2-bromopyrrole, 78307-86-5; 1-(dimethylamino)-2-(2-cyclohexylpropanoyl)pyrrole, 78307-87-6; 2-(2-cyclohexylpropanoyl)-pyrrole, 78307-88-7.

(6) All new compounds reported have been fully characterized by spectral analysis (NMR, IR) and combustion or high-resolution mass spectral analysis.

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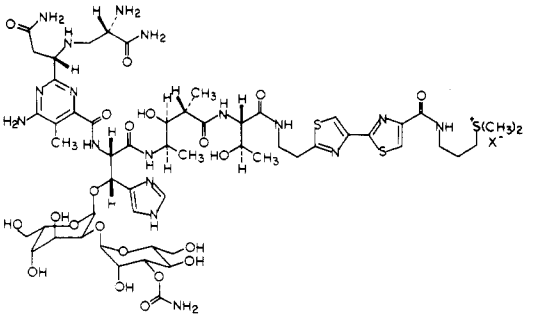
Synthesis of the Carbohydrate Moiety of Bleomycin

Summary: The synthesis of the disaccharide 2-*O*-(3-*O*-carbamoyl-α-D-mannopyranosyl)-L-gulopyranose has been achieved in good yield via the silver triflate promoted coupling of 2,4,6-tri-*O*-acetyl-3-*O*-(*N*-acetylcarbamoyl)-α-D-mannopyranosyl bromide (**7**) with both benzyl 3,4,6-tri-*O*-benzyl-β-L-gulopyranoside (**5**) and 3,4-di-*O*-benzyl-1,6-anhydro-β-L-gulopyranose (**12**).

Sir: Bleomycin A_2 (**1**), one of a family of structurally related antibiotics derived from *Streptomyces*,[1] is the major component of a mixture of bleomycins used clinically for the treatment of certain malignancies.[2] Biochemically,



1

bleomycin mediates the cleavage of DNA, and this property may well constitute the basis for its anticancer activity.[3] To facilitate an understanding of the structural basis of the biological and biochemical activities of the bleomycins, there has been considerable interest in their chemistry, and numerous reports have appeared descriptive of the modification[4] of this natural product as well as the synthesis of components of the bleomycins.[5] Reported herein is the first synthesis of the carbohydrate moiety[6] of bleomycin and certain observations regarding synthetic approaches useful for its elaboration.

Benzyl 3,4,6-tri-*O*-benzyl-β-L-gulopyranoside (**5**) was obtained from L-gulose,[7] the latter of which was acetylated[8] and then converted to 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-β-L-gulopyranose (**2**) via an intermediate tetraacetyl gulopyranosyl bromide (HBr–HOAc, then CH_3OH, $(C_2H_5)_4N^+Br^-$, Hünigs base). Ortho ester **2** was

(1) (a) Umezawa, H. *Lloydia* **1977**, *40*, 67. (b) Konishi, M.; Saito, K.-I.; Numata, K.-I.; Tsuno, T.; Asama, K.; Tsukiura, H.; Naito, T.; Kawaguchi, H. *J. Antibiot.* **1977**, *30*, 789. (c) Umezawa, H.; Muraoka, Y.; Fujii, A.; Naganawa, H.; Takita, T. *Ibid.* **1980**, *33*, 1079. (d) Ohba, K.; Shomura, T.; Tsuruoka, T.; Omoto, S.; Kojima, M.; Hisamatsu, T.; Inouye, S.; Niida, T. *Ibid.* **1980**, *33*, 1236. (e) Shomura, T.; Omoto, S.; Ohba, K.; Ogino, H.; Kojima, M.; Inouye, S. *Ibid.* **1980**, *33*, 1243.

(2) (a) Crooke, S. T. "Bleomycin: Current Status and New Developments"; Carter, S. K., Crooke, S. T., Umezawa, H., Eds.; Academic Press: New York, 1978; p 1 ff. (b) Carter, S. K. *Ibid.* p 9 ff.

(3) Hecht, S. M. "Bleomycin: Chemical, Biochemical and Biological Aspects"; Hecht, S. M., Ed.; Springer-Verlag: New York, 1979; p 1 ff.

(4) For example, see Tanaka, W.; Takita, T. *Heterocycles* **1979**, *13*, 469.

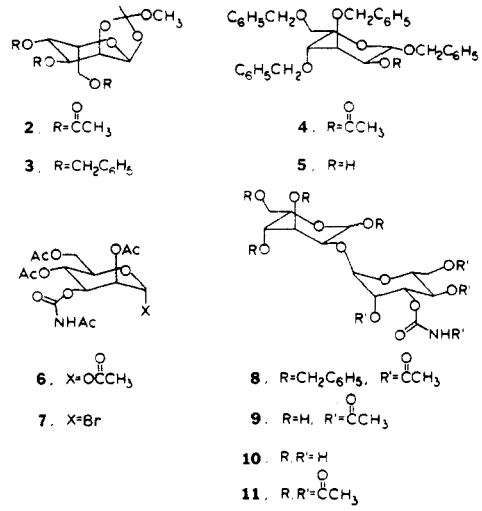
(5) (a) Zee-Cheng, K. Y.; Cheng, C. C. *J. Heterocycl. Chem.* **1970**, *7*, 1439. (b) Takita, T.; Yoshioka, T.; Muraoka, Y.; Maeda, K.; Umezawa, H. *J. Antibiot.* **1971**, *24*, 795. (c) Yoshioka, T.; Muraoka, Y.; Takita, T.; Maeda, K.; Umezawa, H. *Ibid.* **1972**, *25*, 625. (d) Omoto, S.; Takita, T.; Maeda, K.; Umezawa, S. *Carbohydr. Res.* **1973**, *30*, 239. (e) Yoshioka, T.; Hara, T.; Takita, T.; Umezawa, H. *J. Antibiot.* **1974**, *27*, 356. (f) McGowan, D. A.; Jordis, U.; Minster, D. K.; Hecht, S. M. *J. Am. Chem. Soc.* **1977**, *99*, 8078. (g) Minster, D. K.; Hecht, S. M. *J. Org. Chem.* **1978**, *43*, 3987. (h) Hecht, S. M.; Burlett, D.; Mushika, Y.; Kuroda, Y.; Levin, M. D. "Bleomycin: Chemical, Biochemical and Biological Aspects"; Hecht, S. M.; Ed.; Springer-Verlag: New York, 1979; p 48. (i) Hecht, S. M.; Rupprecht, K. M.; Jacobs, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 3982. (j) Levin, M. D.; Subrahamanian, K.; Katz, H.; Smith, M. B.; Burlett, D. J.; Hecht, S. M. *Ibid.* **1980**, *102*, 1452. (k) Umezawa, Y.; Morishima, H.; Saito, S.-I.; Takita, T.; Umezawa, H.; Kobayashi, S.; Otsuka, M.; Narita, M.; Ohno, M. *Ibid.* *102*, 6630. (l) Arai, H.; Hagmann, W. K.; Suguna, H.; Hecht, S. M. *Ibid.* **1980**, *102*, 6631. (m) Takita, T.; Umezawa, Y.; Saito, S.-I.; Morishima, H.; Umezawa, H.; Muraoka, Y.; Suzuki, Y.; Otsuka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1981**, *22*, 671. (n) Ohgi, T.; Hecht, S. M. *J. Org. Chem.* **1981**, *46*, 1232. (o) Hagmann, W. K.; Basha, F. Z.; Hashimoto, M.; Frye, R. B.; Kojo, S.; Hecht, S. M. *J. Org. Chem.* **1981**, *46*, 1413.

(6) The technically simpler synthesis of 2-*O*-(α-D-mannopyranosyl)-L-gulopyranose (i.e., the carbohydrate lacking the carbamoyl moiety of bleomycin) has recently been reported; see Tsuchiya, T.; Miyake, T.; Kageyama, S.; Umezawa, S.; Umezawa, H.; Takita, T. *Tetrahedron Lett.* **1981**, *22*, 1413.

(7) Evans, M. E.; Parrish, F. W. *Carbohydr. Res.* **1973**, *28*, 359.

(8) Isbell, H. S. *J. Res. Natl. Bur. Stand.* **1932**, *8*, 1.

0022-3263/81/1946-3761$01.25/0

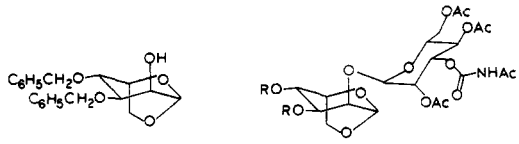


obtained in 31% overall yield from L-gulose as colorless needles, mp 71–2 °C, $[\alpha]^{25}_D$ −22.1° (*c* 1.07, $CHCl_3$),[9] and could be converted directly to benzylated ortho ester **3** (isolated in 57% yield as microcrystals, mp 47.5–48.5 °C, $[\alpha]^{25}_D$ +1.2° (*c* 1.00, $CHCl_3$)) by treatment with C_6H_5C-H_2Cl–KOH, as described.[9,10] Ortho ester **3** was then treated with chlorotrimethylsilane[11] (CH_2Cl_2, reflux, 2 h); crystalline 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-L-gulopyranosyl chloride was obtained in 88% yield, mp 79–80 °C; $[\alpha]^{25}_D$ +58.4° (*c* 0.52, $CHCl_3$).[9] Benzyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-L-gulopyranoside (**4**) ($[\alpha]^{25}_D$ +72.7° (*c* 1.36, $CHCl_3$)) was then obtained in 25% yield as a syrup by treatment of the chloride with $C_6H_5CH_2OH$ (CH_2Cl_2, CF_3SO_3Ag).[12] Deacetylation[13] (CH_3OH, CH_3ONa) then provided key intermediate **5** as colorless microcrystals (95%, mp 62.5–63.5 °C; $[\alpha]^{25}_D$ +48.3° (*c* 0.7, $CHCl_3$)).

The requisite mannose derivative was obtained simply, by treatment of methyl 2,4,6-tri-*O*-acetyl-3-*O*-carbamoyl-α-D-mannopyranoside[5d] with Ac_2O–H_2SO_4 (24 h, 25 °C). The resulting pentaacetate (**6**, obtained as microcrystals from EtOH, mp 135–136 °C; $[\alpha]^{25}$ +23.3° (*c* 1.06, $CHCl_3$))[9] was then converted to the corresponding mannopyranosyl bromide (89%, $[\alpha]^{25}_D$ +78.2° (*c* 1.1, $CHCl_3$), isolated as a white solid foam) via the agency of HBr in HOAc. When **5** and **7** were coupled (CH_2Cl_2, CF_3SO_3Ag, $(CH_3)_2NCON$-$(CH_3)_2$)[14] over a period of 12 h at 25 °C, extractive workup provided the desired disaccharide (**8**) as a colorless syrup (82% yield after chromatographic purification; $[\alpha]^{25}_D$ +46.6° (*c* 0.8, $CHCl_3$)). Hydrogenolysis of **8** over 10% palladium-on-carbon (1 atm of H_2, 24 h) gave 2-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(*N*-acetylcarbamoyl)-α-D-mannopyranosyl]-L-gulopyranose (**9**), isolated as an amorphous solid after chromatographic purification (62% yield): $[\alpha]^{25}_D$ +48.5° (*c* 0.55, MeOH); mass spectrum, M_r 553.[9,15] The α configuration at C-1 of mannose, confirmed by ^{13}C NMR,[16] is consistent with that predicted by the "trans rule".[17] Deblocking of **9** (cat. $^-OCH_3/CH_3OH$, 1 h, 25 °C)[13] provided 2-*O*-(3-*O*-carbamoyl-α-D-mannopyranosyl)-L-gulopyranoside (**10**), the carbohydrate moiety of bleomycin. This species was isolated as an amorphous solid in 96% yield, $[\alpha]^{25}_D$ +65.8° (*c* 0.5, H_2O).[9]

Also prepared from **9** (Ac_2O, pyr, 25 °C, 12 h) was 1,3,4,6-tetra-*O*-acetyl-2-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(*N*-acetylcarbamoyl)-α-D-mannopyranosyl]-α,β-L-gulopyranose (**11**). This species was obtained in 99% yield from **9** as a syrup after extractive workup, $[\alpha]^{25}_D$ +13.9° (*c* 0.6, $CHCl_3$).[9]

An alternate approach to **10** and **11** involved the use of 3,4-di-*O*-benzyl-1,6-anhydro-β-L-gulopyranose (**12**),[5g] a



12 **13**

gulose derivative that might be expected to be less hindered sterically at C-2 than **5**. Coupling of **12** and **7**, in analogy with the transformation **5** + **7** → **8**, provided disaccharide **13** (R = $CH_2C_6H_5$) as a syrup in 68% yield, $[\alpha]^{25}_D$ −78.6° (*c* 0.5, $CHCl_3$).[9] After debenzylation (9:1 EtOH–AcOH, 10% Pd/C, 1 atm of H_2, 24 h; 67%) and acetylation (C_5H_5N–Ac_2O, 25 °C, 24 h; 95%) of this species, treatment with Ac_2O–H_2SO_4 provided **11** ($[\alpha]^{25}_D$ +15.3° (*c* 0.5, $CHCl_3$)).[18] Thus, contrary to the suggestion[6] that "L-gulose[7] and its 3,4-di-*O*-benzyl derivatives[5g]" might not be suitable for the elaboration of dissacharides such as **10**, both **5** and **12** were found to provide the desired compounds in good yield.[19]

It is anticipated that the availability of the fully acetylated disaccharide (**11**) will permit completion of the total synthesis of bleomycin A_2 from synthetic intermediates already in hand.

Acknowledgment. We thank Mr. Jeffrey Shabanowitz and Professor Donald Hunt for assistance in obtaining the mass spectra. This investigation was supported by PHS Grant CA-27603 from the National Cancer Institute, DHHS.

(9) (Partial) ^1H NMR spectra: **2** ($CDCl_3$, $(CH_3)_4Si$) δ 1.71 (s, 3), 2.00 (s, 3), 2.05 (s, 3), 2.12 (s, 3), 3.25 (s, 3), 3.58–3.8 (m, 1), 4.03–4.35 (m, 2), 4.56–4.64 (dd, 1), 5.08–5.42 (m, 2), and 5.50 (d, 1); **3** ($CDCl_3$, $(CH_3)_4Si$) δ 3.23 (s, 3) and 7.22 (m, 15); **4** ($CDCl_3$, $(CH_3)_4Si$) δ 2.17 (s, 3), 3.53 (dd, 1), 3.63 (dd, 1), 3.76 (dd, 1), 4.02 (dd, 1), 4.16 (dt, 1), 4.4–4.65 and 4.85–4.95 (m, 8), 4.95 (d, 1), 5.08 (dd, 1), and 7.2–7.35 (m, 20); **5** ($CDCl_3$, $(CH_3)_4Si$) δ 3.81 (m, 1, H-2), no signal near 2.17; **6** ($CDCl_3$, $(CH_3)_4Si$) δ 2.05 (s, 3), 2.08 (s, 3), 2.17 (s, 6), 2.35 (s, 3), 3.95–4.35 (m, 3), 5.25–5.4 (m, 3), 6.10 (d, 1, J = 2.0 Hz), and 7.82 (b, 1); **7** ($CDCl_3$, $(CH_3)_4Si$) δ 6.29 (d, 1, $J_{1,2}$ = 1.5 Hz, H-1); **8** ($CDCl_3$, $(CH_3)_4Si$) δ 1.95 (s, 3), 2.00 (s, 3), 2.14 (s, 3), 2.42 (s, 3), 3.54 (dd, 1), 3.6 (m, 1), 3.75 (m, 1), 3.83 (dd, 1), 3.92 (dd, 1), 4.15 (dt, 1), 4.27 (m, 1), 4.68 (d, 1), and 5.15–5.25 (m, 3); **11** ($CDCl_3$, $(CH_3)_4Si$) δ 3.94 (dd, 1), 4.98–5.02 (m, 1), 5.00 (d, 1), 5.05 (dd, 1), 5.13 (dd, 1), 5.25 (t, 1), 5.42 (t, 1), 5.88 and 6.27 (2 d, 1, H-1β and H-1α, respectively); **13** (R = $OCH_2C_6H_5$) ($CHCl_3$, $(CH_3)_4Si$) δ 2.07 (s, 3), 2.08 (s, 3), 2.11 (s, 3), 2.43 (s, 3), 3.59 (dd, 1), 3.73 (dd, 1), 3.81 (m, 1), 3.92 (dd, 1), 4.02 (d, 1), 4.44 (t, 1), 4.89 (d, 1), 5.23 (t, 1), 5.31 (dd, 1), and 5.4–5.45 (m, 2); for compound **10**, the mannose H-3 resonated at δ 5.25, in comparison with a value of δ 5.3 for the corresponding proton in bleomycin A_2 (Naganawa, H. In "Bleomycin: Chemical, Biochemical and Biological Aspects"; Hecht, S. M., Ed.; Springer-Verlag: New York, 1979; pp 106–123). In addition satisfactory elemental analyses were obtained for all new solids; syrupy compounds were analyzed by mass spectrometry.

(10) McCloskey, C. M. *Adv. Carbohydr. Chem.* **1957**, *12*, 137 and references therein.

(11) Josephson, S.; Bundle, D. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 297.

(12) The desired β-anomer **4** was separated chromatographically from the (minor) α-anomer prior to conversion to **5**.

(13) Zemplèn, G.; Pacsu, E. *Chem. Ber.* **1929**, *62*, 1613.

(14) Hanessian, S.; Banoub, J. *Methods Carbohydr. Chem.* **1980**, *8*, 247.

(15) This mass spectrum was obtained by fast atom/ion bombardment of the sample dissolved in glycerol doped with LiCl.

(16) Perlin, A. S. In "MTP International Review of Science, Carbohydrates, Organic Chemistry, Series Two", Vol. 7; Aspinall, G. O., Ed.; Butterworths: London, 1976; pp 1–35.

(17) Tipson, R. S. *J. Biol. Chem.* **1939**, *130*, 55.

(18) The two samples of **11** were identical with the exception that the sample derived from **10** was a 1:4 mixture of α- and β-anomers, respectively, while that obtained from **13** was a 15:85 mixture.

(19) Interestingly both glycosidation reactions reported here provided disaccharides in significantly higher yields than the suggested alternative.

(20) On leave from BIOGAL Pharmaceutical Works, Debrecen, Hungary H-4041.

(21) National Cancer Institute Career Development Awardee, 1975–1980.

Registry No. 2, 78418-55-0; 3, 78418-56-1; 4, 78355-18-7; 5, 78355-19-8; 6, 78355-20-1; 7, 78355-21-2; 8, 78355-22-3; 9, 78355-23-4; 10, 78355-24-5; 11 (isomer 1), 78370-94-2; 11 (isomer 2), 78355-25-6; 12, 67965-18-8; 13 (R = $CH_2C_6H_5$), 78355-26-7; L-Gulase, 6027-89-0; tetraacetyl β-L-gulopyranosyl bromide, 78418-57-2; 2-O-acetyl-3,4,6-tri-O-benzyl-β-L-gulopyranosyl chloride, 78355-27-8; methyl 2,4,6-tri-O-acetyl-3-O-carbamoyl-α-D-mannopyranoside, 25217-95-2.

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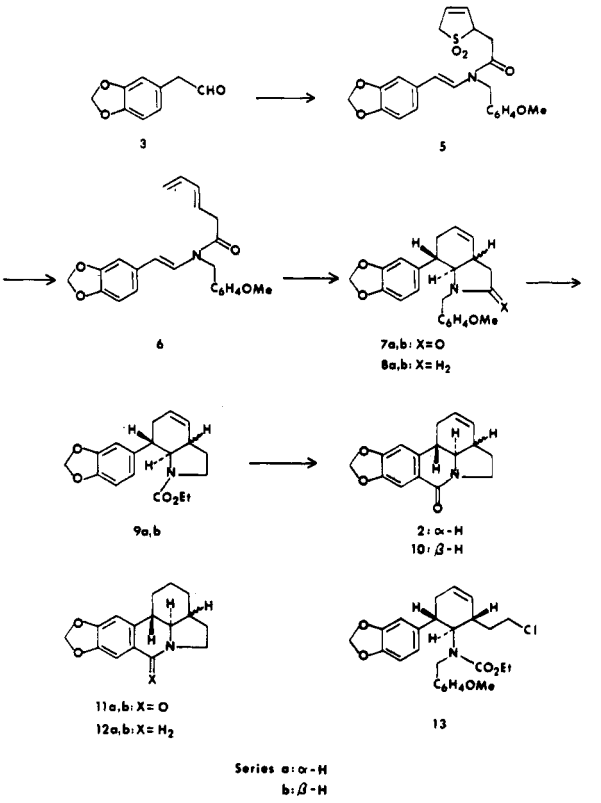
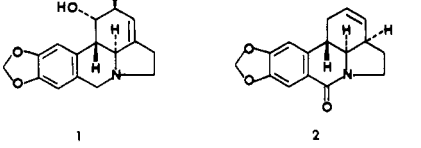
General Strategies for Alkaloid Synthesis via Intramolecular [4 + 2] Cycloadditions of Enamides. Application to the Formal Total Synthesis of Racemic Lycorine[1]

Summary: The application of the intramolecular [4 + 2] cycloaddition of the enamido diene **6** to the construction of the unsaturated oxolycorane **2** is described, thereby completing a novel, formal synthesis of the Amaryllidaceae alkaloid lycorine (**1**).

Sir: The assemblage of functionalized hydroquinolines and hydroindoles, which are structural elements common to many alkaloid natural products, via the intramolecular [4 + 2] cycloadditions[2] of dienamides is firmly established,[3] but the feasibility of employing enamides as dienophiles in [4 + 2] cycloadditions for the construction of these heterocyclic synthons has only been recently recognized.[4,5] Consequently, we now report a novel synthesis of the unsaturated lactam **2** by a route which features the intramolecular cycloaddition of an enamide with an unactivated diene as the key step. Since **2** has been previously converted[6a] to lycorine (**1**),[6,7] an alkaloid of the Amaryllidaceae family,[8] its preparation constitutes the completion of a new, formal synthesis of the title alkaloid.

Scheme I





The trans enamide **5** (mp 73–76 °C; J_{vinyl} = 15 Hz), which bears a diene moiety masked as a dihydrothiophene dioxide, may be readily prepared in 68% overall yield by the condensation of homopiperonal (**3**)[9] with *p*-methoxybenzylamine (toluene, $MgSO_4$, 0 °C, 1 h) followed by acylation of the intermediate imine thus formed in situ with 2-(2,5-dihydro-1,1-dioxothienyl)acetyl chloride (**4**)[4b] in the presence of diethylaniline (1.25 equiv, −78 → 25 °C, 3 h)[10] (Scheme I). Thermolysis of **5** as a 1% solution in refluxing xylene (18 h) containing *O,N*-bis(trimethylsilyl)acetamide (1%) and 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide (0.3%) afforded an inseparable mixture of the two cycloadducts **7a** and **7b** (47%) in a ratio

(1) Portions of this work were previously presented at the Second Chemical Congress of the North American Continent, Las Vegas, NV, August 1980, ORGN 155.

(2) For reviews of intramolecular Diels–Alder reactions, see (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (b) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63.

(3) (a) Oppolzer, W. *J. Am. Chem. Soc.* **1971**, *93*, 3834. (b) Oppolzer, W.; Fröstl, W. *Helv. Chim. Acta* **1975**, *58*, 590. (c) Oppolzer, W.; Fröstl, W.; Weber, H. P. *Ibid.* **1975**, *58*, 593. (d) Oppolzer, W.; Flaskamp, E. *Ibid.* **1977**, *60*, 204. (e) Stork, G.; Morgans, D. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7110.

(4) (a) Martin, S. F.; Desai, S. R.; Phillips, G. W.; Miller, A. C. *J. Am. Chem. Soc.*, **1980**, *102*, 3294. (b) Martin, S. F.; Tu, C.; Chou, T. *Ibid.* **1980**, *102*, 5274.

(5) For a related example, see Stork, G.; Morgans, D. J., Jr. *Tetrahedron Lett.* **1979**, 1959.

(6) For syntheses of lycorine, see (a) Moller, O.; Steinberg, E.-M.; Torssell, K. *Acta Chem. Scand., Ser B.* **1978**, *32*, 98. (b) Tsuda, Y.; Sano, T.; Taga, J.; Isobe, K.; Toda, J.; Takagi, S.; Yamaki, M.; Murata, M.; Iric, H.; Tanaka, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1358. (c) Umezawa, B.; Hoshino, O.; Sowaki, S.; Sashida, H.; Mori, K. *Heterocycles* **1979**, *12*, 1475. (d) Sano, T.; Kashiwaba, N.; Toda, J.; Tsuda, Y.; Irie, H. *Ibid.* **1980**, *14*, 1097.

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(10) The structure assigned to each compound is in accord with its spectral (90-MHz ^1H NMR, ^{13}C NMR, IR, low-resolution mass) characteristics. Analytical samples of all new compounds obtained by recrystallization or chromatography (HPLC) gave satisfactory combustion analysis (C, H, N) and/or appropriate parent ion identification by high-resolution mass spectrometry. All yields reported are of isolated products which were >95% pure. The 90-MHz ^1H NMR data ($CDCl_3$) for several intermediates are as follows. **8a**: δ 7.00 (d, 2 H, *J* = 8 Hz), 6.76 (m, 5 H), 5.86 (s, 2 H), 5.73 (br s, 2 H), 3.73 (s, 3 H), 3.47 (d, 1 H, *J* = 13 Hz), 3.08 (d, 1 H, *J* = 13 Hz), 3.30–1.33 (m, 9 H). **8b**: δ 6.97 (d, 2 H, *J* = 8 Hz), 6.71 (m, 5 H), 5.83 (s, 2 H), 5.77 (br d, 1 H, *J* = 10 Hz), 5.56 (br d, 1 H, *J* = 10 Hz), 3.70 (s, 3 H), 3.13 (d, 1 H, *J* = 13 Hz), 2.60 (d, 1 H, *J* = 13 Hz), 3.03–1.10 (m, 9 H). **9a**: δ 6.70 (m, 3 H), 5.87 (s, 2 H), 5.75 (m, 2 H), 4.13–1.47 (m, 11 H), 1.05 (br t, 3 H, *J* = 7 Hz). **9b**: δ 6.70 (m, 3 H), 5.87 (s, 2 H), 5.77 (m, 2 H), 3.93–1.40 (m, 11 H), 0.90 (t, 3 H, *J* = 7 Hz). **10**: δ 7.57 (s, 1 H), 6.57 (s, 1 H), 5.93 (s, 2 H), 5.75 (m, 2 H), 4.00–3.40 (m, 2 H), 3.17–1.40 (m, 7 H).

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