BULLETIN OF THE CHEMICAL SOCEITY OF JAPAN VOL. 42 2395—2396 (1969)

Syntheses of Pterocarpans. IV.[*1] A New Synthesis of 3,8,9-Trimethoxypterocarpan[*2]

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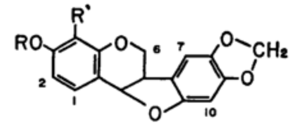
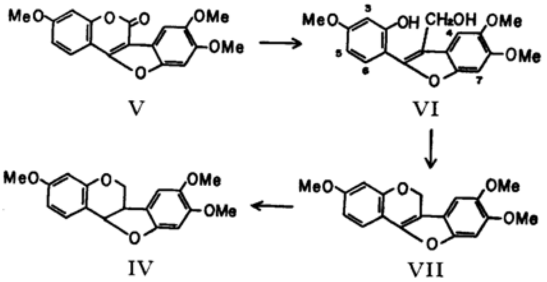
(Received January 24, 1969)

In previous papers, the present authors reported a new method for synthesizing pterocarpans (*e.g.*, (±)-pterocarpin (I),[1] (±)-maackiain (II)[2] and (±)-4-methoxypterocarpin (III)[3]) from the corresponding benzofuro[3′,2′:3,4]coumarins. This paper will describe the synthesis of 3,8,9-trimethoxypteocarpan (IV) from 7,5′,6′-trimethoxybenzofuro[3′,2′ : 3,4]coumarin (V)[4] in a manner similar to that described earlier.[1-3]

The coumarin (V) was subjected to lithium aluminum hydride reduction in refluxing tetrahydrofuran. As expected, the reduction proceeded smoothly, giving the expected product, 5,6-dimethoxy-2-(2-hydroxy-4-methoxyphenyl)-3-hydroxymethylbenzo[*b*]furan (VI), in a 50% yield. The infrared spectrum of VI exhibits absorption bands at 3450 and 3200 cm^{-1} which are attributable to two hydroxyl groups. The diacetate of VI was easily prepared with acetic anhydride in pyridine. The subsequent dehydration of the diol (VI) in boiling diethyleneglycol afforded 3,8,9-trimethoxy-6a,11a-dehydropterocarpan (VII), mp 145—146°C. The NMR spectrum[*3] of VII is closely similar to that of anhydropisatin (*O*-methyl anhydrosophorol) (VIII)[1,5] in having a methylenedioxyl group instead of dimethoxyl groups. Then, VII was hydrogenated in acetic acid with 10% Pd-C to the desired pterocarpan (IV), mp 135—136°C. This substance was found to be identical with an authentic sample which had been obtained by a different route[6] in a mixed melting-point determination and by infrared, ultraviolet, and NMR spectral comparisons.

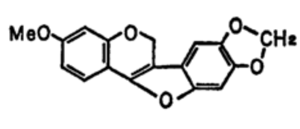


I R=Me, R′=H
II R=R′=H
III R=Me, R′=MeO



V VI

IV VII



VIII

Experimental[*4]

5,6-Dimethoxy-2-(2-hydroxy-4-methoxyphenyl)-3-hydroxymethylbenzo[*b*]furan (V). A suspension of lithium aluminum hydride (300 mg) in anhydrous tetrahydrofuran (50 m*l*) was stirred into a solution of benzofurocoumarin (mp 248—249°C)[4] (IV) (500 mg) in anhydrous tetrahydrofuran (100 m*l*), and the mixture was then refluxed for 1 hr. The excess lithium alumi-

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[*1] Part III: K. Fukui, M. Nakayama and T. Harano, This Bulletin, **42**, 1693 (1969).

[*2] Presented at the Okayama Meeting of the Chemical Society of Japan, Okayama, October, 1967.

1) K. Fukui and M. Nakayama, *Tetrahedron Letters*, **1966** 1805; This Bulletin, **42**, 1408 (1969).

2) K. Fukui, M. Nakayama, H. Tsuge and K. Tsuzuki, *Experientia*, **24**, 536 (1968).

3) K. Fukui, M. Nakayama and K. Tsuzuki, *ibid.*, **25**, 122 (1969).

[*3] The NMR spectra were measured with a Hitachi R-20 spectrometer, using tetramethylsilane as the internal standard (δ-value in $CDCl_3$).

4) a) K. Fukui and M. Nakayama, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **85**, 790 (1964); b) K. Fukui, M. Nakayama and H. Sesita, This Bulletin, **37**, 1887 (1964).

5) a) D. R. Perrin and W. Bottomley, *J. Am. Chem. Soc.*, **84**, 1919 (1962); b) D. D. Perrin and D. R. Perrin, *ibid.*, **84**, 1922 (1962); c) H. Suginome, This Bulletin, **39**, 1525 (1966).

[*4] The melting points are uncorrected. The infrared spectra were measured in Nujol, while the ultraviolet spectra measured in an ethanol solution.

6) a) V. K. Kalra, A. S. Kukla and T. R. Seshadri, *Indian J. Chem.*, **5**, 607 (1967); b) K. Fukui, M. Nakayama and T. Harano, This Bulletin, **42**, 233 (1969).

num hydride was destroyed by the careful addition of ethyl acetate (2 m*l*) and water (50 m*l*). The cooled mixture was acidified with dilute hydrochloric acid and then extracted with ether. After the solvent had been removed under a vacuum, the resulting solid was recrystallized from hot water to give colorless needles of V, mp 130—131°C (250 mg, 50%). IR: 3450, 3200 cm^{-1} (OH). UV: λ_{max} mμ (log ε); 270.5 (4.25), 314 (4.40).

Found: C, 65.21; H, 5.57%. Calcd for $C_{18}H_{18}O_6$: C, 65.44; H, 5.49%.

The diacetate: acetic anhydride - pyridine method; mp 119.5—120.5°C (colorless prisms from methanol). IR: 1788, 1748 cm^{-1} (C=O). NMR:[*3] 7.57 (doublet, *J*=8.5 Hz, C-6′); 7.15 (singlet, C-4); 7.06 (singlet, C-7); 6.93 (quartet, *J*=2.5, 9.0 Hz, C-5′); 6.77 (doublet, *J*=2.5 Hz, C-3′) 5.25 (2H, singlet, $C\underline{H}_2O$); 3.92, 3.90, 3.83 (each 3H, singlet, $C\underline{H}_3O$); 2.07, 2.11 (each 3H, singlet, $C\underline{H}_3CO$).

Found: C, 63.83; H, 5.43%. Calcd for $C_{22}H_{22}O_8$: C, 63.76; H, 5.35%.

3,8,9 - Trimethoxy - 6a, 11a - dehydropterocarpan (VII). A solution of VI (300 mg) in pure diethyleneglycol (10 m*l*) was refluxed for 10 min. During boiling, a slow separation of water was noted. The mixture was then cooled, diluted with water (30 m*l*), extracted with ether, and washed with a 1 N aqueous sodium hydroxide solution. After the ether had been removed under a vacuum, the resulting solid was recrystallized from ethanol to give colorless microcrystals of VII, mp 145—146°C (120 mg, 42%). IR: 1645, 1619, 1589, 1567, 1513, 1491 cm^{-1} (C=C, aromatic). UV: λ_{max} mμ (log ε); 250_i (4.11),[*5] 274 (3.95), 337 (4.39), 355 (4.32).

Found: C, 68.97; H, 5.28%. Calcd for $C_{18}H_{16}O_5$: C, 69.22: H, 5.16%.

3,8,9-Trimethoxypterocarpan (IV). A mixture of VII (100 mg) and 10% Pd-C (40 mg) in acetic acid (100 m*l*) was shaken in an atmosphere of hydrogen until 1.1 mol of hydrogen had been absorbed. After the catalyst had then been removed, the filtrate was evaporated under a vacuum. The resulting solid was recrystallized from ethanol to give colorless needles of IV (50 mg, 50%); mp 135—136°C (lit, mp 138—139°C;[6a] mp 136—137°C[6b]), identical with that of an authentic sample.[6b]

[*5] i=inflection point.