Communications to the Editor

Chem. Pharm. Bull.
31(11)4193—4194(1983)

PHOTOCHEMICAL REARRANGEMENT OF PSEUDOANISATIN AS AN α-HYDROXY KETONE

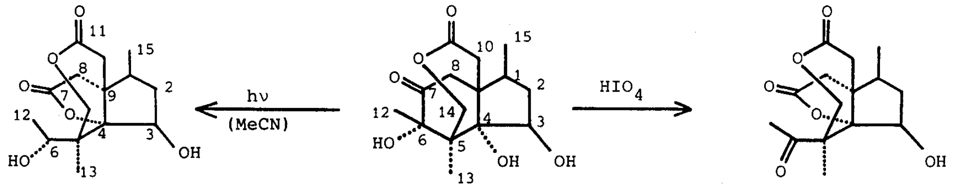
Isao Kouno and Nobusuke Kawano*
Faculty of Pharmaceutical Sciences, Nagasaki University, Bunkyo-cho, Nagasaki 852

Photo-induced Norrish type I cleavage of pseudoanisatin (1) as an α-hydroxy ketone, followed by γ-lactone formation is reported. The structure (2) of the rearrangement product was deduced on the basis of its spectral and chemical evidences.

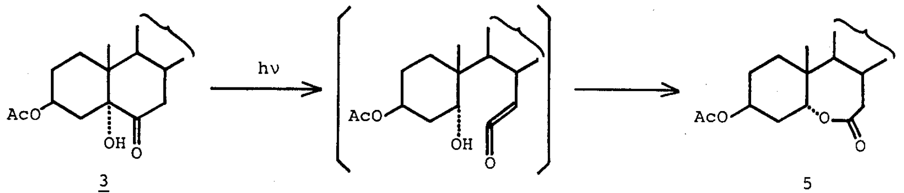
KEYWORDS——photochemical rearrangement; pseudoanisatin; α-hydroxy ketone; γ-lactone; ^{1}H-NMR spectra; ^{13}C-NMR spectra

Recently, we reported[1] the revised structure (1) of pseudoanisatin, $C_{15}H_{22}O_6$, a sesquiterpene lactone from Japanese star anise (*Illicium anisatum L.*). A novel base catalyzed rearrangement of 1 was also reported[2] to give a translactonization product including steric inversion at C-3 and C-4 and hemiacetal formation. This paper deals with photochemical rearrangement of 1 which has an α-hydroxy ketone group.

As far as we know the only report of photochemical rearrangement of α-hydroxy ketones is that of R. C. Cookson and his co-workers.[3] 3β-Acetoxy-5α-hydroxy-cholestan-6-one (3) and its 5β-epimer (4) on UV irradiation in an ethanol solution underwent carbon bond α-cleavage between C-5 and C-6 to form ε-lactones (5 and 6). Ketenes can be considered a possible intermediate in the course of these rearrangements.



2 1 7



3
4 (5β-epimer)

5
6 (5β-epimer)

Pseudoanisatin (1) gave a photochemical rearrangement product (2) in good yield on UV irradiation through a Pyrex filter in its acetonitrile solution. 2, mp 194-195°C showed an ion peak at m/z 299 (M+1) and the following ^{1}H-NMR signals (δ-values in a $CDCl_3$ solution): 0.83 (3H, s, Me-13), 1.14 (3H, d, J=6.8 Hz, Me-15), 1.52 (3H, d, J=6.4 Hz, Me-12), and 5.52 (1H, q, J=6.4 Hz, H-6),[4] indicating carbon bond cleavage between C-6 and C-7. The presence of the partial structure, $\text{Me-}\underset{|}{\text{C}}\text{H-O-}$ was

Table 1. ^{13}C-NMR Spectral Data of Compounds, 1, 2, and 7

Assigned carbon	1 (C_5D_5N)	2 ($CDCl_3$)	7 (C_5D_5N)
Me-12	18.37	17.39	27.60
-13	13.76(a)	14.47(a)	18.56(a)
-15	13.92(a)	15.82(a)	18.80(a)
CH_2-2	43.83(b)	42.91	44.53
-8	35.22	35.00	36.03
-10	43.07(b)	39.12	40.34
-14	69.57	66.43	70.25
CH-1	40.20	46.16	48.04
-3	78.18	75.46	79.78
C-9	47.73	49.47	49.68
-4	84.68	98.28	96.95
-5	48.82	50.44	57.27
-6	79.26 s	79.05 d	208.22 s
-7	206.54	175.87	175.88
-11	174.25	172.89	172.00

s:singlet, d:doublet, (a) and (b) mean that the assignments may be reversed.
JEOL FX-90Q was used.

confirmed by double irradiation techniques between the two signals of δ 1.52 and 5.52. The ^{13}C-NMR spectral data (Table 1) are also compatible with the structure showing a doublet signal at δ 79.05.

However, the lactone formed seems not to be ε-lactone, but γ-lactone because the IR spectrum of 2 showed a new absorption band at 1780 cm^{-1}(γ-lactone) in addition to the original one at 1725 cm^{-1}. Therefore, it was deduced that lactone formation between the hydroxy group at C-4 and the ketene group gave the product (2). Previously, one of us reported[5] an oxidation product of 1 with sodium periodate. The structure of the oxidation product is now deduced to be the formula (7).[6] The ^{13}C-NMR spectral data of 7 are also given in Table 1. The C-4 signals of 2 and 7 showed considerable low field shifts in comparison with that of 1, suggesting a lactone formed with the hydroxy group at C-4. Reduction of 7 with sodium borohydride gave two compounds, one of them was identified with 2 (mixed mp, ^{1}H-NMR, TLC, and IR).

As regards the configuration of the secondary hydroxy group formed by cleavage, Cookson et al. reported[3] the retention of the original configuration. Accordingly, also in our case the configuration of C-6 was deduced as shown in the formula (2), keeping the original configuration.

REFERENCES AND NOTES

1) I. Kouno, H. Irie, N. Kawano, and Y. Katsube, Tetrahedron Lett., 24, 771(1983).
2) I. Kouno, H. Irie, N. Kawano, T. Taga, and K. Osaki, Chem. Lett., 1983, 1323.
3) R. C. Cookson, R. P. Gandhi, and R. M. Southam, J. Chem. Soc.(C), 1968, 2494.
4) The data other than given in the text are as follows: 2.42 and 2.79(1H, d, each J=18.4 Hz), 2.65 and 3.28(1H, d, each J=13.9 Hz), 3.51 and 4.03(1H, d, each J= 11.3 Hz), 2.05 - 2.40(2H, m), 4.10(1H, m), 4.60(1H,br d, J=5.0 Hz), and 5.24 (1H, br s).
5) M. Okigawa and N. Kawano, Tetrahedron Lett., 1971, 75.
6) Discussions on the structure will be given in a full paper.

(Received September 12, 1983)