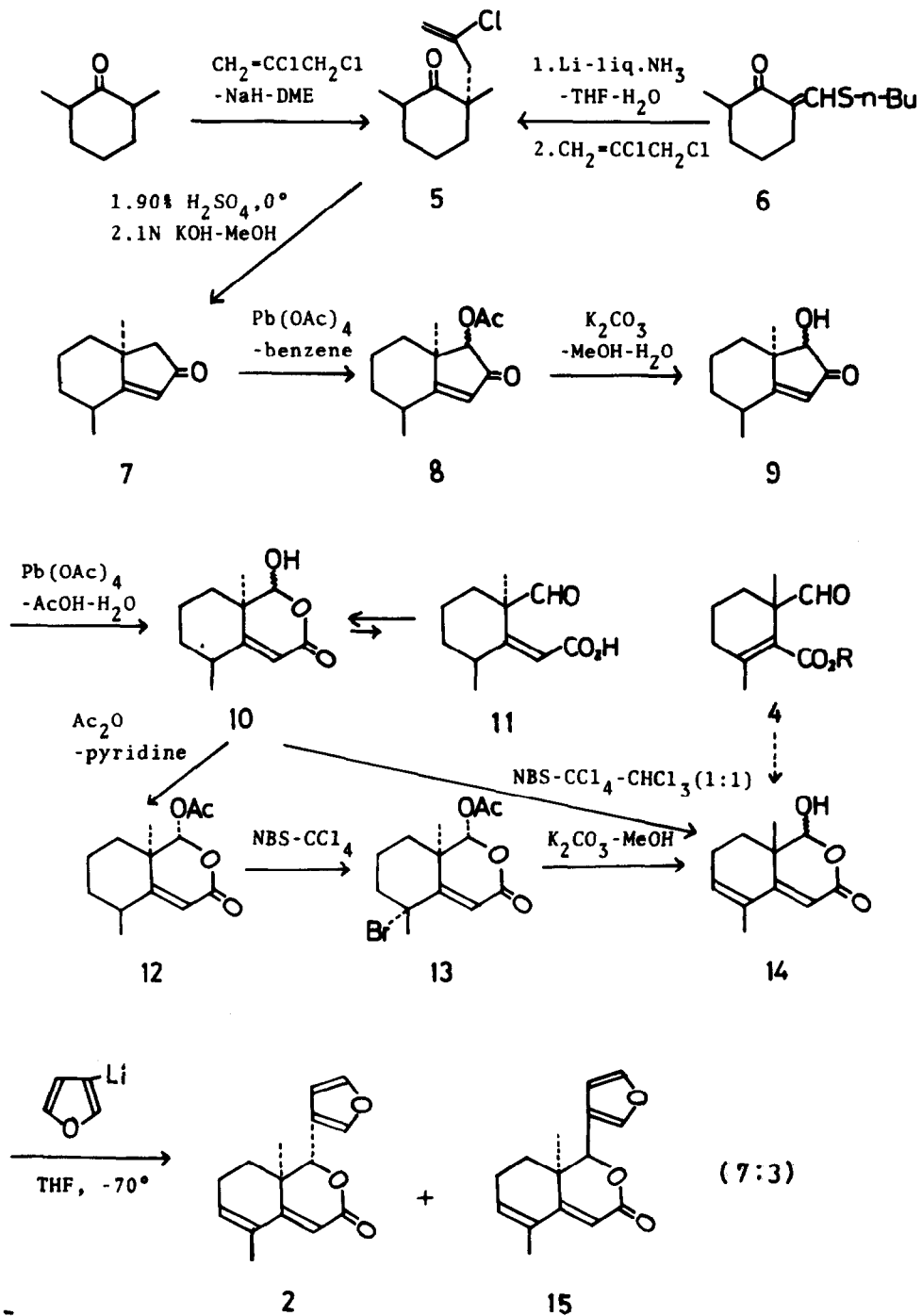




(1H, d,  $J=2$  Hz), by hydrolysis with 90% sulfuric acid at  $0^\circ$  for 10 min, followed by the intramolecular aldol condensation with 1N methanolic potassium hydroxide in 89% overall yield. 7 is assumed to have more stable conformation as depicted. The acetoxylation of 7 with lead tetraacetate at refluxing temperature afforded the epimeric mixture of  $\alpha$ -acetoxyketones 8, which, without further purification, was hydrolyzed with potassium carbonate in aq. methanol (1:3) to yield the corresponding mixture of ketols 9<sup>8</sup>, m.p.  $101-103^\circ$ ,  $\nu_{\max}$  3440, 1695 and  $1600\text{ cm}^{-1}$ , in 74.4% yield. The ketols 9 could not be cleaved with periodic acid, but readily transformed by the agency of lead tetraacetate in aq. acetic acid to the epimeric mixture of the lactols 10 in 93.5% yield: m.p.  $150-151^\circ$ ;  $\nu_{\max}$  3320, 1700, 1620 and  $990\text{ cm}^{-1}$ ;  $\delta^{\text{CDCl}_3}$  1.20 and 1.26 (3H in total, each s), 1.16 (3H, d,  $J=6$  Hz), 5.30 (1H, s), 5.76 and 5.80 (1H in total, each d,  $J=1.2$  and 1.5 Hz respectively)<sup>9</sup> The inspection of IR and NMR spectra indicates the absence of the corresponding aldehyde-carboxylic acid form 11. Upon acetylation with acetic anhydride-pyridine 10 furnished the single acetate 12, m.p.  $121-122^\circ$ ,  $\nu_{\max}$  1770, 1730, 1610 and  $1030\text{ cm}^{-1}$ ,  $\delta^{\text{CDCl}_3}$  1.26 (3H, s), 1.16 (3H, d,  $J=7$  Hz), 2.18 (3H, s), 6.16 (1H, s) and 5.82 (1H, d,  $J=2$  Hz), of which acetoxy group is presumably  $\alpha$ -oriented. When the lactol 10 was brominated with N-bromosuccinimide in a mixture of carbon tetrachloride and chloroform, the diene lactol 14 was obtained in 64% yield. On the other hand the similar treatment of the acetate 12 resulted in the formation of the brominated product 13. 13 was transformed to 14 by the treatment with potassium carbonate in methanol. Finally the diene lactol 14 was treated with 3-furyllithium in tetrahydrofuran, conveniently prepared from 3-bromofuran<sup>2</sup>, at  $-70^\circ$  and then at room temperature for 48 hr to provide d1-pyroangolensolide 2, m.p.  $145-145.5^\circ$  (1-form<sup>3</sup>  $149^\circ$ );  $m/e$  244 ( $M^+$ ), 148, 133, 105 and 95;  $\lambda_{\max}^{\text{EtOH}}$  277 nm ( $\epsilon$  19300);  $\nu_{\max}^{\text{CHCl}_3}$  1710, 1630, 1600, 1500 and  $880\text{ cm}^{-1}$ ;  $\delta^{\text{CDCl}_3}$  1.04 (3H, s), 1.88 (3H, d,  $J=2$  Hz), 2.28 (2H, m), 5.14 (1H, s), 5.88 (1H, s), 6.20 (1H, m), 6.50 (1H, m) and 7.52 (2H, m), and its diastereomer 15, m.p.  $138-140^\circ$ ;  $m/e$  244 ( $M^+$ ), 148, 133, 105, 95 and 91;  $\lambda_{\max}^{\text{EtOH}}$  278 nm ( $\epsilon$  17300);  $\nu_{\max}^{\text{CHCl}_3}$  1710, 1630, 1600, 1500 and  $870\text{ cm}^{-1}$ ;  $\delta^{\text{CDCl}_3}$  1.38 (3H, s), 1.90 (3H, d,  $J=2$  Hz), 2.30 (2H, m), 5.14 (1H, s), 5.94 (1H, s), 6.18 (1H, m), 6.32 (1H, m) and 7.44 (2H, m) in a ratio of 7:3 in 50% yield. Although the direct comparison of the synthetic product with the



authentic specimen is not yet performed, the melting point and the spectral data of the former are consistent with those reported for pyroangolensolide<sup>3</sup>.

The synthesis of calodendrolide from the intermediates prepared in this work is now under investigation.

#### REFERENCES AND NOTES

1. Part III of a series of the investigations titled as "Synthetic Studies on Terpenoid Compounds". Ref. 2 is read as Part I and for Part II, cf. K. Matsuo, T. Tokoroyama and T. Kubota, Chemistry Letters, 397 (1973).
2. Y. Fukuyama, T. Tokoroyama and T. Kubota, Tetrahedron Letters, 3401 (1972).
3. J. B. Davis, V. M. Godfrey, K. Jewers, A. H. Manchanda, F. V. Robinson and D. A. H. Taylor, Chemistry and Industry, 201 (1970).
4. J. M. Cassady and C. -S. Liu, Chem. Comm., 86 (1972).
5. K. Jewers, A. H. Manchanda and D. A. H. Taylor, Chemistry and Industry, 976 (1972).
6. R. M. Coates and R. L. Sowerby, J. Am. Chem. Soc., 93, 1027 (1971).
7. R. E. Ireland and R. C. Kierstead, J. Org. Chem., 31, 2543 (1966).
8. Satisfactory elemental analyses were obtained for all new crystalline compounds reported herein.
9. The ratio between the epimers is approximately 1:1 as estimated from the NMR spectrum.