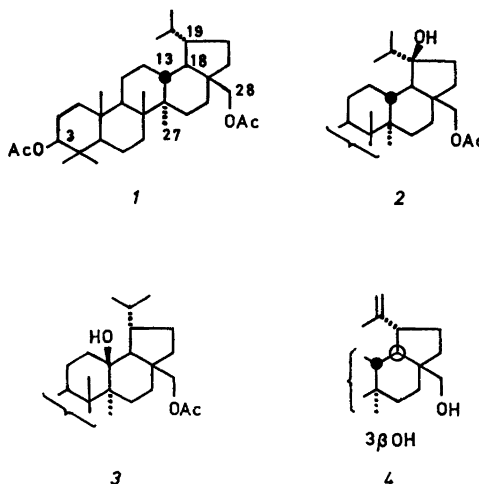


18. Andrewes, A. G., Liaaen-Jensen, S. and Weeks, O. B. *Acta Chem. Scand. B* 29 (1975) 884.
19. Hertzberg, S., Borch, G. and Liaaen-Jensen, S. *Acta Chem. Scand.* 32 (1978). *In press.*
20. Bodea, C., Andrewes, A. G., Borch, G. and Liaaen-Jensen, S. *Phytochemistry. In press.*
21. Buchecker, R. and Eugster, C. H. *Helv. Chim. Acta* 54 (1971) 327.
22. Fiksdahl, A., Mortensen, T. and Liaaen-Jensen, S. *J. Chromatogr. In press.*
23. Buchecker, R. and Eugster, C. H. *Helv. Chim. Acta* 56 (1973) 1124.
24. Andrewes, A. G., Borch, G. and Liaaen-Jensen, S. *Acta Chem. Scand. B* 28 (1974) 139.
25. Buchecker, R., Hamm, P. and Eugster, C. H. *Helv. Chim. Acta* 57 (1974) 631.
26. Nitsche, H. *Arch. Mikrobiol.* 95 (1974) 79.

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rigid stereostructure, to the environmental diversity of carbon centres, and to the opportunity of selective functionalisation within the fully saturated carbon skeleton — a tedious task by other means. In this field the dry ozonation of a friedelane hydrocarbon was very recently reported<sup>1b</sup> to yield compounds resulting from oxidation at secondary carbons. A higher selectivity is shown<sup>1</sup> by substrates containing polar groups, which regulate the orientation of the molecule on the adsorbent and thus direct the spatial attack of ozone.

We now report that the dry ozonisation of 3 $\beta$ ,28-diacetoxylupane (*1*) on silica gel yields only one product (conversion ca. 10%). Its IR spectrum showed the presence of a hydroxyl group and the <sup>1</sup>H NMR spectrum revealed its tertiary nature. The protons at C-28 appeared at exceptionally low field in the <sup>1</sup>H NMR spectrum indicating that the new hydroxyl is located in the neighbourhood of C-28.



## Dry Ozonation of 3 $\beta$ , 28-Diacetoxylupane. A Comment on the Structure of a Pentacyclic Triterpenoid Lactone from *Dillenia indica* (Linn.)

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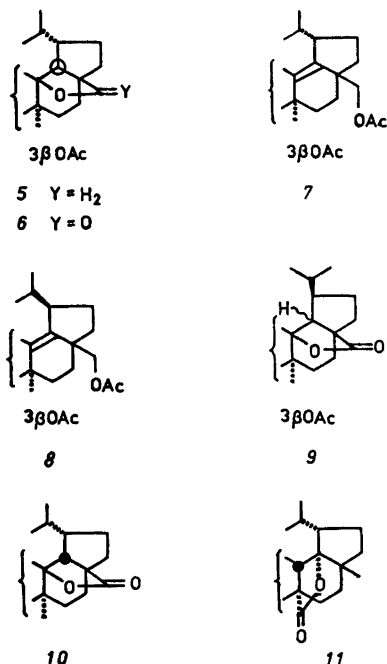
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Recently dry ozonation — *i.e.* the ozonation of a substrate adsorbed on a carrier (*e.g.* silica gel) without solvent — has been found to be a valuable tool for functionalisation at an unactivated carbon.<sup>1</sup> This oxygenation is often remarkably regioselective and stereospecific with retention of configuration. Usually oxidation at a tertiary carbon to give an alcohol is preferred but attack at secondary carbons may also occur.

Triterpenes are an interesting group for testing this functionalisation method due to their

The suitable tertiary positions on the  $\beta$ -face are at C-13 and C-19. The physical constants of the ozonation product are in rather good agreement with the known<sup>2</sup> 19 $\beta$ -hydroxy compound *2* and differs clearly from those reported<sup>3</sup> for the 13 $\beta$ -hydroxy compound *3*. There was, however, some doubt about the correctness of the reported<sup>3</sup> structure of *3* and therefore we have prepared both of these hydroxy diacetates *2* and *3* for identification. The 19 $\beta$ -hydroxy compound *2* is available<sup>2</sup> from betulin (*4*) and the 13 $\beta$ -hydroxy compound *3* was prepared from the known<sup>4</sup> ether *5* via NaIO<sub>4</sub>-RuO<sub>2</sub> oxidation to the lactone *6*, LiAlH<sub>4</sub> reduction and reacylation to the hydroxy diacetate *3*. The hydroxy diacetate from the dry ozonation of 3 $\beta$ ,28-diacetoxylupane (*1*) was found to be identical (m.p., mixed m.p.,  $[\alpha]_D$ , TLC, IR, <sup>1</sup>H NMR, *m/e*) with the 19 $\beta$ -hydroxy derivative *2*.

The lactone **6** is reported<sup>3</sup> to occur in Nature. The physical constants of our synthetic lactone **6** differ significantly, however, from those reported<sup>3</sup> for the natural compound. The same applies to the hydroxy diacetate prepared from the natural lactone and **3** prepared from the synthetic lactone **6**. Therefore at least the stereostructure of the natural compound appears to be at fault. The direct comparison<sup>5</sup> of



the acetates of the natural and synthetic lactone showed very similar TLC behaviour (a minor difference in colour after an H<sub>2</sub>SO<sub>4</sub> spray was observed). The mass spectra showed significant differences but the overall similarity indicates that these two compounds are closely related possibly stereoisomers. Olefin **7** is reported<sup>3</sup> as a major fraction in BF<sub>3</sub>-induced dehydration of the hydroxy diacetate derived from the natural lactone. We have prepared the isomeric olefin **8** via a non-dehydrative route, and the physical constants for **7** and **8** are notably different. Thus the (19 $\alpha$ H) configuration **9** is excluded for the natural lactone, although, less emphasis should probably be given to the dehydration result, as isomerisation reactions may intervene under the BF<sub>3</sub> conditions. If the 28 $\rightarrow$ 13 lupanolide structure is indeed correct for the natural lactone, the above arguments imply that this lactone has the highly crowded (18 $\beta$ H), (19 $\beta$ H) structure **10**. An alternative possibility for the natural lactone is the 27 $\rightarrow$ 18 olide structure **11**.

*Experimental.* For general information see

Ref. 6. The <sup>1</sup>NMR spectra were recorded in CDCl<sub>3</sub> solution and the IR spectra using KBr pellets.

*Dry ozonisation of 3 $\beta$ ,28-diacetoxylupane (1).* 3 $\beta$ ,28-Diacetoxylupane (**1**) (0.5 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and silica gel (50 g) was added. The solvent was removed *in vacuo* and the silica saturated with ozone at -80 °C and then allowed to reach room temperature during 4 h. Extraction and chromatography on silica plates (CHCl<sub>3</sub> eluent) gave starting material and 3 $\beta$ ,28-diacetoxy-19 $\beta$ -hydroxylupane (**2**) (0.05 g), m.p. (EtOH) 265 °C, [ $\alpha$ ]<sub>D</sub> +18° (c 0.9) (Ref. 2, m.p. 272-273 °C, [ $\alpha$ ]<sub>D</sub> +19°.)  $\bar{\nu}$  3520, 1735, 1715;  $\delta$  4.5 (1 H, m, 3 H), 4.4 (2 H, br. s, 28-CH<sub>2</sub>); M<sup>+</sup> 544.

*The  $\gamma$ -lactone of 3 $\beta$ -acetoxy-13 $\beta$ -hydroxylupane-28-oic acid (6).* 3 $\beta$ -Acetoxy-13 $\beta$ ,28-epoxylupane<sup>4</sup> (**5**) (0.2 g) in CCl<sub>4</sub> (25 ml) and NaIO<sub>4</sub> (0.5 g) in H<sub>2</sub>O (25 ml) and a catalytic amount of RuO<sub>2</sub> were shaken vigorously overnight. Work-up and crystallisation from EtOH gave the  $\gamma$ -lactone of 3 $\beta$ -acetoxy-13 $\beta$ -hydroxylupane-28-oic acid (**6**) (0.13 g) m.p. 240 °C, [ $\alpha$ ]<sub>D</sub> +1.2° (c 0.84);  $\bar{\nu}$  1755, 1720;  $\delta$  4.5 (1 H, m), 2.05 (3 H, s); M<sup>+</sup> 498.

*3 $\beta$ ,28-Diacetoxy-13 $\beta$ -hydroxylupane (3).* Lactone **6** (0.1 g) was reduced with LiAlH<sub>4</sub> in boiling Et<sub>2</sub>O, worked up and reacylated by refluxing 10 min in Ac<sub>2</sub>O (3 ml). 3 $\beta$ ,28-Diacetoxy-13 $\beta$ -hydroxylupane (**3**) (0.05 g) crystallised on cooling m.p. 230 °C, [ $\alpha$ ]<sub>D</sub> -8° (c 0.5);  $\bar{\nu}$  3520, 1730, 1725;  $\delta$  4.5 (1 H, m), 3.95 and 4.7 ( $\delta$  1 H, d, J = 12 Hz), 2.05 (6 H, s); M<sup>+</sup> absent, M<sup>+</sup> - 60 484.

*3 $\beta$ ,28-Diacetoxy-(19 $\alpha$ H)-lup-13(18)-ene (8).* 3 $\beta$ ,28-Diacetoxylupa-12,18-diene<sup>6</sup> (0.2 g) was hydrogenated over PtO<sub>2</sub> (0.1 g) as reported<sup>7</sup> previously for the corresponding lupane derivative. Work-up and crystallisation from EtOH gave 3 $\beta$ ,28-diacetoxy-(19 $\alpha$ H)-lup-13(18)-ene (**8**) (0.16 g) m.p. 166 °C, [ $\alpha$ ]<sub>D</sub> -43° (c 1.0);  $\bar{\nu}$  1730, 1240;  $\delta$  4.5 (1 H, m), 3.95 (2 H, br. s), 2.8-2.1 (3 H, m) 2.05 (6 H, s); M<sup>+</sup> 526.

- a. Beckwith, A. L. J. and Duong, T. *Chem. Commun.* (1978) 413; b. Akiyama, E., Tada, M., Tsuyuki, T. and Takahashi, T. *Chem. Lett.* (1978) 305, and references therein.
- Allison, J. M., Lawrie, W., McLean, J. and Taylor, G. R. *J. Chem. Soc.* (1961) 3353.
- Banerji, N., Majumder, P. and Dutta, N. L. *Phytochemistry* 14 (1975) 1447.
- Vystrčil, A. and Protiva, J. *Collect. Czech. Chem. Commun.* 39 (1974) 1382.
- We thank Dr. Nilima Banerji for a sample of the natural lactone from *Dillenia indica* (Linn.).
- Suokas, E. and Hase, T. *Acta Chem. Scand. B* 31 (1977) 231.
- Suokas, E. and Hase, T. *Acta Chem. Scand. B* 31 (1977) 633.

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