Lupan-3β,20-diol and Lupan-3β,20,28-triol in Bark from Birch, *Betula verrucosa* Erh.

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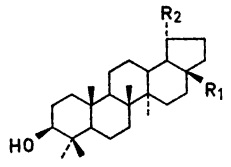
The triterpene [1] present in prevailing amounts in birch bark is betulinol (I), minor constituents [2] being lupeol (II), betulinic acid (III), and allobetulinol. With the exception of allobetulinol, these terpenes are lupane derivatives. Allobetulinol has a carbon skeleton which is formed from lupane derivatives by rearrangement. This paper describes the isolation of two additional lupane derivatives from the bark.

The neutral extractives from bark of *Betula verrucosa* Erh. were acetylated and acetate mixture was chromatographed on silica gel. The presence of lupeol acetate, betulinol diacetate, and two compounds, below called *A* and *B*, were shown.



	R1	R2	
I	$-CH_2OH$	$-C(CH_3)=CH_2$	Betulinol
II	$-CH_3$	$-C(CH_3)=CH_2$	Lupeol
III	$-COOH$	$-C(CH_3)=CH_2$	Betulinic acid
IV	$-CH_3$	$-C(OH)(CH_3)_2$	Monogynol A
V	$-CH_2OH$	$-C(OH)(CH_3)_2$	

Compound *A* was identified as 3β-acetoxy-lupan-20-ol (the 3β-acetate of IV) by comparison with an authentic sample. The corresponding diol (IV) has previously been obtained from two other plant species [3,4] and named monogynol A.[3]

Compound *B* analysed for $C_{34}H_{56}O_5$ [= $C_{30}H_{49}(OH)(OCOCH_3)_2$]. Its IR spectrum showed ester and hydroxyl peaks. The hydroxyl group(s) were probably tertiary since they had not been acetylated.

The mass spectrum of compound *B* was identical with that of betulinol acetate. As lupeol acetate (the acetate of II) and 3β-acetoxy-lupan-20-ol (the 3β-acetate of IV) have identical spectra, compound *B* might be 3β,28-diacetoxy-lupan-20-ol (the 3β-acetate of V). This assumption was confirmed by the preparation of *B* from 3β,28-diacetoxy-20,29-epoxy-lupan.

To our knowledge, lupan-3β,20,28-triol has not previously been isolated from a natural source.

Experimental. Isolation of the triterpenes. Birch bark was extracted with ethanol. The ethanolic solution was evaporated and the residue recrystallised from ethanol. The crystals consisted of impure betulinol (*cf.* Ref. 5). The mother liquor was evaporated and the residue was acetylated with acetic anhydride and pyridine (1:1, v/v) at room temperature. The acetylated material (300 mg) was fractionated by preparative TLC on silica gel using isopropyl ether-light petroleum (1:1, v/v) as solvent (spray reagent, Rhodamine 6G [6,7]). The following fractions were collected:

Fraction *1* (30 mg). After recrystallisations from methanol it had the properties: m.p. 213–215°C, $[\alpha]_{578}$ + 30° ($CHCl_3$). The material, which was not further purified, consisted mainly of lupeol acetate as shown by TLC, argentative TLC, and GLC (according to Ref. 7).

Fraction *2* (130 mg). It consisted mainly of betulinol diacetate.

Fraction *3* (80 mg). After recrystallisations from hexane it yielded compound *A* with the following properties: $[\alpha]_{578}$ + 15° and $[\alpha]_{364}$ + 50° (*c* 1.0, $CHCl_3$): m.p. 252–260°, undepressed on admixture with an authentic sample of 3β-acetoxy-lupan-20-ol (m.p. 252–257°, $[\alpha]_D$ + 16°).[8]

The mass spectra of compound *A*, authentic 3β-acetoxy-lupan-20-ol, and lupeol acetate were identical. No peak was observed for the molecular ion of 3β-acetoxy-lupan-20-ol (below called M^+). Some of the peaks were: *m/e* 468 (M^+ minus H_2O) (70 % of the base peak), 425 (4 %), 412 (5 %), 357 (10 %), 249 (the *g* fragment) [9] (17 %), 189 (83 %), and 43 (the base peak).

Fraction *4* (10 mg). In order to obtain a larger amount of this fraction, the separation of the bark extractives was repeated on a silica gel column. Recrystallisations from acetonitrile and light petroleum yielded compound *B* which had the following properties: ν_{max} at 1728 and 3500 cm^{-1} (KBr): $[\alpha]_{578}$ + 2° and $[\alpha]_{364}$ + 5° (*c* 0.25, $CHCl_3$), m.p. 253–256°C, undepressed on admixture with syn-

thetic 3β,28-diacetoxy-lupan-20-ol (see below). (Found: C 75.5; H 10.1; O 14.5. Calc. for $C_{34}H_{56}O_5$: C 75.0; H 10.4; O 14.7).

The mass spectra of compound *B*, synthetic 3β,28-diacetoxy-lupan-20-ol and betulinol diacetate were identical. No peak was observed for the molecular ion of 3β,28-diacetoxy-lupan-20-ol (below called M^+). Some of the peaks were: *m/e* 526 (M^+ minus H_2O) (15 % of the base peak), 511 (the base peak), 453 (11 %), 423 (14 %), 249 (the *g* fragment [9]) (8 %), and 189 (58 %).

Synthesis of 3β,28-diacetoxy-lupan-20-ol. 3β,28-Diacetoxy-20,29-epoxy-lupan [10] (1.0 g, m.p. 200–217°C) was reduced with lithium aluminium hydride as described for the synthesis of lupan-3β,20-diol from the corresponding epoxide.[4] The reduced material was acetylated with pyridine and acetic anhydride at room temperature. The product (0.58 g) was purified by TLC (silica gel, 1 % methanol in isopropyl ether) and recrystallisations from acetonitrile and hexane: m.p. 253–256°C, $[\alpha]_{578}$ + 4° (c 0.5, $CHCl_3$) (0.10 g, yield 10 %). (Found: C 75.0; H 10.4. Calc. for $C_{34}H_{56}O_5$: C 75.0; H 10.4).

Its proton magnetic resonance spectrum agreed with the structure (V) (*cf.* Ref. 11): δ 0.85 ppm (strong singlet), 4α, 4β and 10-CH_3: δ 1.03 ppm (singlet), 14-CH_3: 1.10 ppm (singlet), 8-CH_3: δ 1.15 and 1.25 ppm (two singlets), 21- and 22-CH_3: δ 3.90 and 4.44 ppm (two doublets, J_c = 11 cps), 28-H: δ 4.57 ppm (triplet, J_c = 7 cps), 3α-H.

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Halogenation of Ketones

V.* Studies on the Mechanisms of Base Catalyzed Halogenations of Butanone-2

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In 1904 it was proposed by Lapworth that the rate determining step in the acid catalyzed halogenation of ketones is the enolization of the ketone.[1] Later, the same author proposed the same step as being rate determining in the base catalyzed reaction.[2] In 1932 Watson and Yates proposed that the base catalyzed halogenation of ketones involves both the enolate anion and the enol.[3] The currently accepted view is that halogenation of ketones can proceed by either an acid or a base catalyzed reaction, the enolization or formation of the enolate anion being the rate determining step in both cases.[4-10]

In a recent paper the present author gave the first experimental evidence for *two* different mechanisms for the base catalyzed halogenation of ketones.[11] In that paper the sodium acetate and sodium bicarbonate catalyzed chlorination and bromination of butanone-2 were studied. The products were analyzed by NMR and the value of the ratio 3-halogenation/1-halogenation (K_{Hal}-values) were determined. In these weak base catalyzed reactions these values

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