Tetrahedron, 1964, Vol. 20, pp. 1983 to 1985. Pergamon Press Ltd. Printed in Northern Ireland

CHEMISTRY OF THE EUPHORBIACEAE—IX[1]

FURTHER CONSTITUENTS OF BEYERIA LESCHENAULTII

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(*Received* 27 *April* 1964)

Abstract—A new diterpene diol has been isolated from *Beyeria leschenaultii* (D.C.) Bail. and has been shown to be (−)-kaur-16-ene-3α,19-diol (Ia) by its relation to the known 16α-(−)-kaurane-3α,17,19-triol (II) which also occurs in this plant.

THE ether-soluble neutrals from *B. leschenaultii* were subjected to chromatography on alumina and the first-eluted major component was found to be lup-20-ene-3β, 16β-diol.[2] Subsequent elution afforded two diterpenes, one of which was identified as 16α-(−)-kaurane-3α,17,19-triol (II) previously obtained from the neutral constituents of a *Beyeria sp. nov.*[3] The other diterpene constituent, $C_{20}H_{32}O_2$, and its readily formed diacetate (Ib) showed IR absorption at 3070, 875 cm^{-1} characteristic of a vinylidene group. The NMR spectrum* of the diacetate showed signals attributable to a vinylidene group (5·24τ), an axial acetoxymethyl group centred at 5·76τ(J, 12 c/s),[4] and two quaternary methyl groups (8·94, 9·00τ). Absorption at 5·44τ(1H,W½17 c/s) required an equatorial secondary acetoxyl group.

The presence of the primary and secondary hydroxyl groups in the diol was confirmed by oxidation by the Jones reagent[5] to the aldehydo-ketone (IIIa) whose NMR signal at 0·25τ was consistent with that of axial aldehyde groups.[6] The aldehydo-ketone reacted with acid or alkali to give the norketone (IIIb) whose NMR spectrum (CCl_4) indicated the presence of one quaternary (8·8τ) and one tertiary (9·08τ; J,7 c/s) methyl group. This degradation is most readily explained by a 1:3 relationship of the hydroxyl groups in the diol, and this was supported by the ready formation of an ethylidene derivative.

The diacetate was ozonized to give formaldehyde and the norketodiacetate (Ic) which was hydrolysed to the keto-diol (Id) whose IR absorption at 1735 cm^{-1} was expected for a cyclopentanone.

At this stage the diol was reasonably formulated as (Ia). The configurational assignments were confirmed as follows. The ethylidene derivative of the diol was hydroborated, by attack from the less hindered side, to the primary alcohol (IVa) possessing the 16β-hydroxymethyl group. This was oxidized by the Jones reagent to the corresponding acid (IVb) which was methylated to the ester (IVc). The ester

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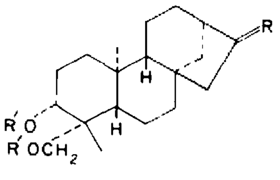
* NMR spectra were measured with a Varian A60 spectrometer in $CDCl_3$ solution unless otherwise stated.

[1] Part VIII. C. A. Henrick and P. R. Jefferies, *Austr. J. Chem.* **17**, in the press.
[2] G. V. Baddeley, A. J. Bealing, P. R. Jefferies and R. W. Retallack, *Austr. J. Chem.* in the press.
[3] G. V. Baddeley, M. W. Jarvis, P. R. Jefferies and R. S. Rosich, *Austr. J. Chem.* **17**, 578 (1964).
[4] P. Beak and E. Wenkert, *Tetrahedron Letters*, 358 (1961).
[5] K. Bowden, I. M. Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.* 39 (1946).
[6] R. A. Laidlaw and J. W. W. Morgan, *J. Chem. Soc.* 644 (1963).

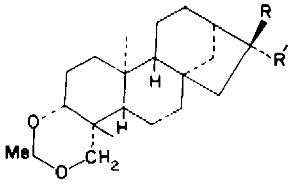
was subjected to equilibration catalysed by sodium methoxide to give, as the major product, methyl 3α,19-ethylidenedioxy-16α-(−)-kauran-17-oate (IVd). This ester is of established configuration and was previously obtained from the triol (II).[3]

Beyeria leschenaultii provides an interesting example of the rare co-occurrence of di- and triterpenes.



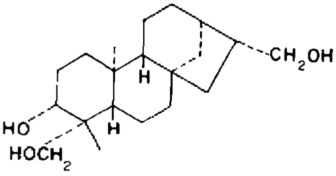
I

	R	R′
(a)	CH_2	H
(b)	CH_2	$COCH_3$
(c)	O	$COCH_3$
(d)	O	H

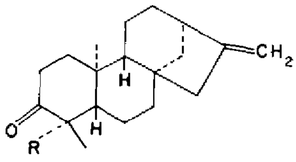


IV

	R	R′
(a)	CH_2OH	H
(b)	CO_2H	H
(c)	CO_2Me	H
(d)	H	CO_2Me



II



III

	R
(a)	CHO
(b)	H

EXPERIMENTAL*

Isolation of the diterpenes of Beyeria leschenaultii

After elution of lup-20-ene-3β,16β-diol,[2] further elution with benzene–ether (5:1) gave (−)-*kaur-16-ene-3α,19-diol* (Ia, 16g) as prisms (from ethyl acetate), m.p. 184–85°, $[\alpha]_D$ −66°(*c*, 1·66) (Found: C, 78·7; H, 10·6. $C_{20}H_{32}O_2$ requires: C, 78·9; H, 10·6%). Further elution with benzene–ether (2:1) gave 16α-(−)-kaurane-3α,17,19-triol (II, 2g) as prisms from ethanol–ethyl acetate, m.p. and m.m.p. with an authentic sample 248–249°. The IR spectra of the two samples were identical.

The *diacetate* (Ib) was prepared by the acetic anhydride–pyridine method and crystallized from methanol–water as plates m.p. 113–114°, $[\alpha]_D$ −66° (*c*, 1·95) (Found: C, 74·3; H, 9·3. $C_{24}H_{36}O_4$ requires: C,74·2; H, 9·3%).

3,19-*Dioxo*-(−)-*kaur*-16-*ene* (III*a*)

The diol (90 mg) in acetone (25 ml) was treated with the Jones reagent (0·5 ml) for 10 min. The excess of oxidant was destroyed (ethanol) and the product isolated through ether to give the aldehydo-ketone (73 mg) as needles (from ethanol–water) m.p. 125–126°, $[\alpha]_D$ −35° (*c*, 1·25) (Found: C, 80·1; H, 9·4. $C_{20}H_{28}O_2$ requires: C, 79·9; H, 9·4%).

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* For general experimental details see Ref. 2.

19-*Nor*-(−)-*kaur*-16-*en*-3-*one* (IIIb)

(i) The aldehydo-ketone (80 mg) reacted with H_2SO_4 in acetone (1%; 20 ml) during 15 hr to give the norketone as needles from ethanol, m.p. and m.m.p., with the ketone obtained below, 102–103°.

(ii) The aldehydo-ketone (280 mg) reacted with ethanolic KOH (5%; 30 cc) during 1 hr to give the norketone (240 mg) as needles (from ethanol) m.p. 102–103°, $[\alpha]_D$ −106° (*c*, 1·73) (Found: C, 83·6; H, 10·1: $C_{19}H_{28}O$ requires: C, 83·8; H, 10·4%).

3α,19-*Ethylidenedioxy*-(−)-*kaur*-16-*ene*

The diol (200 mg) in ether (30 ml) was shaken with paraldehyde (1·2 ml) and HCl aq (0·5 ml) for 2 hr. The crude product was dissolved in light petroleum and filtered through alumina (neutral Act IV; 5 g) to give the ethylidene derivative (180 mg) as needles (from ethanol) m.p. 176–177°, $[\alpha]_D$ −39° (*c*, 1·48) (Found: C, 80·0; H, 10·3. $C_{22}H_{34}O_2$ requires: C, 80·0; H, 10·4%).

3α,19-*Diacetoxy*-17-*nor*-(−)-*kauran*-16-*one* (Ic)

A solution of the diacetate (Ib, 116 mg) in ethyl acetate (25 ml) was saturated with ozone at −15°. Water was added and the mixture heated under reflux for 45 min, and distilled. The distillate reacted with dimedone to give formaldehyde dimethone (26 mg; 35%) m.p. and m.m.p. 189°. The non-volatile residue was dissolved in light petroleum–benzene (2:1) and filtered through alumina to give the norketo-diacetate (98 mg) as needles from ethanol–water, m.p. 127–128°, $[\alpha]_D$ −20° (*c*, 1·16) (Found: C, 70·7; H, 8·9. $C_{23}H_{34}O_5$ requires: C, 70·7; H, 8·8%).

17-*Nor*-(−)-*kaur*-16-*one*-3α,19-*diol* (Id) was prepared from Ic by hydrolysis with ethanolic KOH (5%). The product formed plates from ethanol–water, m.p. 203–204°, $[\alpha]_D$ −21° (*c*, 1·11) (Found: C, 74·2; H, 9·7. $C_{19}H_{30}O_3$ requires: C, 74·5; H, 9·9%). ν max. 1735 cm^{-1}.

3α,19-*Ethylidenedioxy*-16β-(−)-*kauran*-17-*ol* (IVa)

The ethylidene derivative of the diol (617 mg) with $LiAlH_4$ (1 g) in tetrahydrofuran (100 ml) at 0°, was treated dropwise with BF_3 (4 ml) in tetrahydrofuran (80 cc) with continuous stirring during 2·5 hr. The mixture was stirred for a further 30 min when the excess of $LiAlH_4$ was destroyed by the addition of ethyl acetate. Sodium hydroxide (4N; 60 ml) and H_2O_2 (30%; 7 ml) were then added and the mixture left for 15 hr. Isolation through ether gave a crude product which was dissolved in light petroleum–benzene (1:1) and filtered through alumina (neutral Act III; 10 g) to give the alcohol (540 mg) as needles from benzene–light petroleum, m.p. 181–182°, $[\alpha]_D$ −5° (*c*, 1·38) (Found: C, 76·1; H, 10·3. $C_{22}H_{36}O_3$ requires: C, 75·8; H, 10·4%).

3α,19-*Ethylidenedioxy*-16β-(−)-*kauran*-17-*oic acid* (IVb)

The alcohol (IVa; 490 mg) in acetone (80 ml) was treated with the Jones reagent (3 ml) for 15 min. Ethanol was added, the mixture concentrated under red. press. and extracted with ether. The required acid was removed from the organic layer by 0·5N NaOH, the alkaline solution re-acidified and extracted with ether to give the acid (IVb; 430 mg) as prisms from ethanol, m.p. 296–297° (dec.) $[\alpha]_D$ −22° (*c*, 1·03) (Found: C, 72·6; H, 9·4. $C_{22}H_{34}O_4$ requires: C, 72·9; H, 9·5%).

The *methyl ester* (IVc), prepared by treatment with an excess of ethereal diazomethane, formed plates from ethanol–water, m.p. 154–155°, $[\alpha]_D$ −26° (*c*, 1·10) (Found: C, 73·5; H, 9·8. $C_{23}H_{36}O_4$ requires: C, 73·4; H, 9·6%).

Epimerization of the ester (IVc)

The ester (480 mg) was added to CH_3ONa (from 200 mg Na) in anhydrous methanol (60 ml). The mixture was heated under reflux for 60 hr, poured into water, and extracted with ether. The organic layer was extracted with 0·5N NaOH aq, the alkaline solution acidified and extracted with ether to give an acidic product which was esterified by diazomethane in ether to give IVd as prisms from ethanol–water, m.p. and m.m.p. with an authentic sample 202–203° $[\alpha]_D$ −34° (*c*, 1·06). The IR and NMR spectra of the two samples were identical. Lit.[8] gives m.p. 202–203°, $[\alpha]_D$ −33°.