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NEW PENTACYCLIC DITERPENE ACID
TRACHYLOBAN-19-OIC ACID FROM SUNFLOWER

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Abstract—A new trachylobane derivative—trachyloban-19-oic acid (IIIa) together with the biogenetically related (−)-kaur-16-en-19-oic acid (Ia) was isolated from the flowers of *Helianthus annuus* L. The structure for the title compound was determined by degradation and spectral data.

TETRA- and pentacyclic diterpenoids probably have a common biogenetic origin.* Only one example is known of the co-occurence of tetracyclic-kaurene and pentacyclic-trachylobane derivatives. This is in Trachylobium (Cesalpiniaces)[4] and it is also the first isolation of trachylobane diterpenoids. Another natural source of trachylobane derivatives has been found in *Helianthus annuus* L. (Compositae) and a new trachyloban-19-oic acid (IIIa) was isolated together with (−)-kaur-16-en-19-oic acid (Ia). The presence of diterpene acids in Compositae is exceptional.

(−)-*Kaur*-16-*en*-19-*oic acid* (Ia). The saponified ether extract yielded a mixture of two very weak acids. These were separated as their methyl esters into two crystalline, GLC and TLC homogeneous, isomeric ($C_{20}H_{29}COOCH_3$) methyl esters. The more strongly absorbed compound was identified as Ia in the following way:

The C_{20} structure, with two singlet C—Me signals in the PMR spectrum indicated a diterpenoid compound. The presence of the typical "methylene" bands in the IR spectrum and two olefinic proton signals at 4·73 δ in the PMR spectrum agreed with a probable kaurene skeleton. The characteristic pattern of the bands in the region 1150–1250 cm^{-1} in the IR spectrum of the methyl ester (Ib) and its hydrogenation product (IIa), suggested an axial carbomethoxyl group.[5] Methyl (−)-kaur-16-en-19-oate (Ib)[6] is one of the possible structures. This was confirmed by LAH reduction to the primary alcohol Ic,[6] catalytic reduction to methyl (−)-kauran-19-oate (IIa) and its further reduction to the primary alcohol IIb.[7]

Trachyloban-19-*oic acid* (IIIa), *skeleton.* The second methyl ester isolated had no "end absorption" in the UV spectrum, and as the IR and PMR also showed no unsaturation, a pentacyclic diterpene monocarboxylic acid methyl ester was indicated. The known trachyloban-18-oic acid[4] was excluded because of distinctly different properties of its methyl ester (m.p. 112°, $[\alpha]_D$ −41°), as compared with m.p. 98–100°, $[\alpha]_D$ −70·5° for the pentacyclic acid isolated. The parent hydrocarbon was obtained

* Wenkert biogenetic scheme[1] employs nonclassical carbonium ion arising from protonated tricyclic pimaradiene. This ion might collapse to tetracyclic kaurene, atisine and stachene skeletons or cyclize to pentacyclic trachylobane.[2,3]

via the standard transformations IIIb, IIIc, IIIf, IIIg (LAH reduction, CrO_3–pyridine oxidation, Wolff-Kizner reduction) and had properties identical with those reported for trachylobane.[4]

Trachyloban-19-oic acid (IIIa), *position of the carboxyl group.* The 1150–1250 cm^{-1} region in the IR spectrum of this methyl ester indicated an axial orientated carbomethoxyl group, as in Ib and IIa.[5] The AB quartet in the PMR spectrum of the primary alcohol IIIc and its acetate (IIId) is typical of an axial CH_2OR group[8] (Table 1). The identity of chemical shifts and coupling constants confirmed the same position of the carboxyl group in both acids. The calculated molecular optical rotation differences of $COOCH_3$—CH_3 and CH_2OH—CH_3 for this trachylobane acid derivative and the 4-axial substituted kaurene are nearly the same (Table 2).

Table 1. AB quartets of CH_2OH and CH_2OAc groups in PMR spectra of kaurene, kaurane and trachylobane 19-(axial)-alcohols, c/s from TMS

Compound	A	B	Δ	J_{AB}	CH_3COO—
Ic in $CDCl_3$	223·1	204·9	18·2	11·0	—
IIb in $CDCl_3$	222·6	205·4	17·2	11·0	—
IIIc in $CDCl_3$	222·5	205·5	17·0	11·0	—
Id in $CDCl_3$	252·9	232·1	20·8	11·2	121·5
IIc in $CDCl_3$	252·5	231·5	21·0	11·0	121·0
IIId in $CDCl_3$	252·5	231·5	21·0	11·0	121·0
Id in C_6H_6	255·5	230·5	25·0	11·0	105·5
IIc in C_6H_6	259·1	233·4	25·7	11·0	105·0
IIId in C_6H_6	258·3	232·7	25·4	11·0	104·0

Table 2. Molecular optical rotation differences

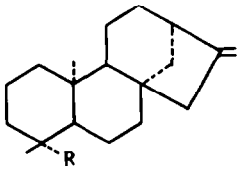
Compound		$[M]_D$	$[M]_D$–$[M]_D$ of hydrocarbon
Methyl trachyloban-19-oate	IIIb	−2290°	−1120°
Trachyloban-19-ol	IIIc	−1090	+80
Trachyloban	IIIg	−1170	
Methyl (−)-kaur-16-en-19-oate	Ib	−3280	−1100
(−)-Kaur-16-en-19-ol	Ic	−2220	−40
(−)-Kaur-16-en		−2180	

The above data excluded the other possible position of the carboxyl group at C-10 in this trachylobane acid.

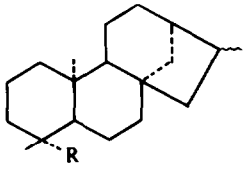
Finally, the methyl ester IIIb was transformed to the atisiren-19-oate (IV), the structure of which was confirmed by its IR and PMR spectra, characteristic for the CH—C(=CH_2)—CH_2 group and its m.p. as reported.[3]

EXPERIMENTAL

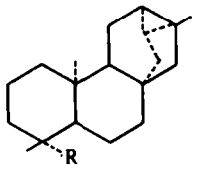
The ether extract (85 g) of dry sunflower flowers (800 g) was saponified (KOH 55 g, MeOH 300 ml, benzene 50 ml and water 50 ml, 4 hr under reflux). Dilution with water, acidification with excess of AcOH gave after ether extraction 65·8 g of the saponified fraction. Aliphatics were clathrated by dissolving in boiling MeOH (650 ml) with urea (200 g). The residue from the filtrate was taken up in ether, washed with water and Na_2CO_3 aq. This extraction removed the nonclathrated fatty acids leaving most of the diterpene acids in the neutral fraction (33·1 g). Column chromatography on 300 g of silica gel (for TLC without gypsum) separated the diterpene acids from the triterpene alcohols; benzene : ether mixture (9 : 1) eluted 9·0 g of acids.



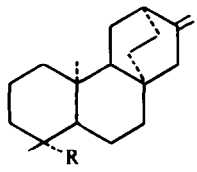
Ia: R = COOH
Ib: R = $COOCH_3$
Ic: R = CH_2OH
Id: R = CH_2OOCCH_3



IIa: R = $COOCH_3$
IIb: R = CH_2OH
IIc: R = CH_2OOCCH_3



IIIa: R = COOH
IIIb: R = $COOCH_3$
IIIc: R = CH_2OH
IIId: R = CH_2OOCCH_3
IIIe: R = CH_2O—TOSYL
IIIf: R = CHO
IIIg: R = CH_3



IV: R = $COOCH_3$

Part of this material was methylated with etheral diazomethane (long reaction time required). TLC on silica gel (at least two developments in benzene : light petroleum, 1 : 3) or better TLC "argentation chromatography" on silica gel impregnated with 30% of $AgNO_3$ (the same as previous developing system) revealed the presence of two components. They were separated on 200 g of silica gel (for TLC) impregnated with 30 g of $AgNO_3$, elution with benzene gave 2·4 g of less and 3·4 g of the more polar component.

Methyl (−)-*kaur*-16-*en*-19-*oate* (Ib). Crystallization of the more polar fraction from dilute MeOH gave 2·9 g of pure Ib, m.p. 73·5–74·5°, $[\alpha]_D$ −104° (in $CHCl_3$), reported[6] m.p. 71–73°. (Found: C, 79·74· 79·52; H, 10·39, 10·32. $C_{21}H_{32}O_2$ requires: C, 79·70; H, 10·19%): GLC–MS (SE-30 column, single peak): 316 (M^+ base peak), 301, 284, 274, 273, 269, 257, 256, 241, 213; IR: (KBr plate): 3100 w, 1660 m, and 880 s (methylene), 1720 s (ester carbonyl), 1240 s, 1230 s, 1205 s, 1192 s and 1150 s cm^{-1} (axial carbomethoxyl group); PMR: δ in $CDCl_3$ 4·73 bs 2H, 3·62 s 3H, 1·16 s 3H, 0·83 s 3H, in C_6H_6 4·90 bs 2H, 3·40 s 3H, 0·83 s 3H.

Methyl (−)-*kauran*-19-*oate* (IIa). Hydrogenation of Ib (in AcOH, Pd-C 5%, one mole of H_2 absorbed) gave after crystallization from dil MeOH a mixture of 16-epimeric kaurane esters, m.p. 65–77°, $[\alpha]_D$ −75° (in $CHCl_3$). (Found: C, 79·56, 79·34; H, 11·01, 10·82. $C_{21}H_{34}O_2$ requires: C, 79·19; H, 10·76%); IR (KBr plate): 1720 s (ester carbonyl), 1240 s, 1220 s, 1190 s and 1160 s cm^{-1} (axial carbomethoxyl group); PMR: δ in $CDCl_3$ 3·53 s 3H, 0·98 d J = 6 3H, 0·82 s 3H, in C_6H_6 3·38 s 3H, 1·11 s 3H, 1·03 d 3H J = 6, 0·86 s 3H.

(−)-*Kaur*-16-*en*-19-*ol* (Ic). LAH reduction of Ib in boiling THF gave a quantitative yield of Ic, which was crystallized from dil MeOH, m.p. 143–144·5°, $[\alpha]_D$ −78° (in $CHCl_3$), reported[6]: m.p. 141–143°, $[\alpha]_D$ −77°. (Found: C, 83·63; H, 11·44. $C_{20}H_{32}O$ requires: C, 83·27; H, 11·18%); IR: (KBr plate): 3090 w, 1655 m, 880 s (methylene), 3420 s, 1020 s (OH); PMR: δ in $CDCl_3$ 4·90 bs 2H, ABq (Table 1), 1·00 s 3H, 0·95 s 3H; acetate Id: m.p. 113–118°; PMR: δ in $CDCl_3$ 4·73 bs 2H, ABq (Table 1), 2·02 s 3H, 1·04 s 3H, 0·96 s 3H; in C_6H_6 4·82 bs 2H, ABq (Table 1), 1·76 s 3H, 0·92 s 6H.

(−)-*Kauran*-19-*ol* (IIb). This was obtained from IIa (as Ic), m.p. 146–151°, $[\alpha]_D$ −33°, reported[7] m.p. 146·5°; IR (KBr plate): 3420 s, 1035 s, 1020 s and 1010 s cm^{-1} (hydroxyl); acetate IIc: PMR δ in $CDCl_3$ ABq (Table 1), 2·00 s 3H, 1·02 and 0·92 9H: in C_6H_6 ABq (Table 1), 1·75 s 3H, 0·56 9H.

Methyl trachyloban-19-oate (IIIb). The less polar fraction from the silver nitrate impregnated silica gel column was crystallized from dil MeOH to give 1·8 g of IIIb, m.p. 98–100°, $[\alpha]_D$ −70·5° (in $CHCl_3$). (Found: C, 79·86, 79·96, 79·81; H, 10·30, 10·26, 10·40. $C_{21}H_{32}O_2$ requires: C, 79·70; H, 10·19%); GLC–MS (SE-30 column single peak): 316 (M^+ base peak), 301, 284, 274, 260, 257, 256, 245, 241, 201; IR (KBr plate): 1725 s (ester carbonyl) 1225 s, 1240 s, 1200 s, 1162 s, 1155 s, (axial carbomethoxyl group); PMR: δ in $CDCl_3$ 3·60 s 3H, 1·12 s 6H, 0·75 s 3H, 0·6 m, in C_6H_6 3·33 s 3H, 1·13 s 3H, 1·08 s 3H, 0·85 s 3H, 0·55 m, UV: no appreciable absorption.

Trachyloban-19-ol (IIIc). LAH reduction of IIIb in boiling THF gave IIIc, which was crystallized from dil MeOH, m.p. 130–131°, $[\alpha]_D$ −38° (in $CHCl_3$); (Found: C, 83·30, 83·56; H, 10·96, 11·24. $C_{20}H_{32}O_2$ requires: C, 83·27; H, 10·18%); IR (KBr plate): 3430 s, 1035 s and 1022 s cm^{-1} (hydroxyl); PMR: δ in $CDCl_3$ ABq (Table 1), 1·12 s 3H, 0·92 s 6H, 0·6 m; acetate IIId: m.p. 94–96°; PMR: δ in $CDCl_3$ ABq (Table 1), 1·98 s 3H, 1·08 s 3H, 0·90 s 3H, 0·87 s 3H, 0·6 m; in C_6H_6 ABq (Table 1), 1·73 s 3H, 1·18 s 3H, 0·90 s 3H, 0·65 m; tosylate IIIe m.p. 123–125°.*

19-*Oxotrachyloban* (IIIf). CrO_3–pyridine oxidation of IIIc gave after chromatography on silica gel a 45% yield of IIIf; IR (nujol): 2700 m, 2350 m and 1719 s cm^{-1} (aldehyde); semicarbazone m.p. 211°.

Trachyloban (IIIg). The Wolff-Kizner reduction of the hydrazone (or semicarbazone) of IIIf (4 hr under reflux with KOH in diethylene glycol at 200–210°) resulted in a 60% yield of IIIg, m.p. 44–47°, $[\alpha]_D$ −43·2° (in $CHCl_3$), reported[4]: m.p. 45–46°, $[\alpha]_D$ −43°. (Found: C, 88·45; H, 12·08. $C_{20}H_{32}$ requires: C, 88·16; H, 11·84%; IR (KBr plate): 2950 s, 2870 s, 1470 s, 1450 s, 1392 m, 1372 m, 970 m and 843 m cm^{-1}; PMR: δ in $CDCl_3$ four 3H singlets at 1·125, 0·940, 0·825 and 0·800, cyclopropane protons multiplet at 0·65; reported[4]: 1·13 s, 0·94 s, 0·835 s, 0·80 s and 0·65 m.

Methyl atisiren-19-oate (IV). Methyl trachyloban-19-oate (IIIb; 60 mg) in 2 ml ethyl ether (2 ml), cyclohexane (6 ml) and trifluoacetic acid (2 ml) was kept at 0° for 20 hr. A mixture of products was separated on silver nitrate impregnated silica gel plates (benzene as developing system) into unchanged IIIb and IV (about 30%). The latter crystallized from dil MeOH, m.p. 125–128°, reported[3] m.p. 126–127°; IR (KBr plate): 3080 w, 1645 m and 880 m (methylene), 1720 s (ester carbonyl), 1230 s, 1210 m, 1190 s, 1170 s, 1150 m and 1145 m cm^{-1} (axial carbomethoxyl group); PMR: δ in $CDCl_3$ 4·77 bqt J = 2 c/s, 4·55 bqt J = 2 c/s both 1H, 3·64 s 3H, 2·25 m 1H, 1·95 m 2H, 1·17 s 3H and 0·80 s 3H (similar as reported for atisirene.[3,4]

Measurements. PMR spectra were taken on a Varian HA-60/IL. Mass spectra were determined on a LKB-9000 spectrometer.

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* LAH reduction of tosylate IIIe was unsuccessful for the preparation of parent hydrocarbon. The hydrocarbon obtained in poor yield was probably hexacyclic (due to C-19, C-20 cyclization) showing the presence of two Me groups only in PMR spectrum.