Acetonide of ent-7α,18,19-trihydroxykaur-16-ene. The triol (40 mg) in Me_2CO (3 ml) was treated with $CuSO_4$ (240 mg) at room temp. for 5 hr. The soln was filtered, the solvent was evapd and the residue chromatographed on Si gel in EtOAc–petrol (3:7) to afford the acetonide as a gum. (Found: 360.2647, $C_{23}H_{36}O_3$ requires 360.2664; 345.2429, M-15, $C_{22}H_{33}O_3$ requires 345.2429). PMR ($CDCl_3$): δ 0.93 (3H, *s*, 20-H_3) 1.30 and 1.35 (each 3H, *s*, C.Me_2), 3.21 and 5.54 (each 1H, *d*, J = 12 Hz, CH_2O) 3.60 (3H, *br s*, CH_2O and CH.OH), 4.77 (2H, *br s*, $=CH_2$); MS *m/e*: 360, 345 (100%), 342, 327, 272, 257, 254, 239, 226, 211.

Reduction of methyl ent-7,18-dihydroxykaur-16-en-19-oate. The methyl ester (6 mg) in dry Et_2O (3 ml) was added to a suspension of LiAlH (25 mg) in the same solvent (5 ml). After 6 hr H_2O and dil.HCl were carefully added and the product was recovered in Et_2O to afford the triol (3 mg) which was identified by TLC and its PMR spectrum.

Epicandicandiol-[18-^3H]. *ent*-7α-Acetoxykaur-16-en-18-al (20 mg) [8] was added to a soln of NaB^3H_4 (1.5 mg, 10 mCi) in MeOH (3 ml). After 2 hr the MeOH was evapd, Et_2O (5 ml) was added followed by excess LiAlH. After a further 3 hr H_2O and dil.HCl were added and the product was recovered in Et_2O, to afford epicandicandiol-[18-^{3}H] (18 mg, 3.0878 mCi).

Acknowledgement—We thank the Fundaçion Juan March for financial assistance.

REFERENCES

1. Hanson, J. R. and White, A. F. (1968) *Tetrahedron* **24**, 6291.
2. (a) Bearder, J. R., MacMillan, J., Wels, C. M. and Phinney, B. O. (1975) *Phytochemistry* **14**, 1741;
2. (b) Bearder, J. R., Frydman, V. M., Gaskin, P., MacMillan, J., Wels, C. M. and Phinney, B. O. (1976) *J. Chem. Soc. Perkin* 1 173.
3. Cross, B. E., Galt, R. H. B. and Hanson, J. R. (1963) *J. Chem. Soc.* 3783.
4. Hanson, J. R. (1971) in *Progress in the Chemistry of Organic Natural Products* (Herz, W., Grisebach, H. and Kirby, G. W. eds) Vol. 29, p. 395. Springer-Verlag, Vienna.
5. Breton, J. L., Gonzales, A. G., Rocha, J. M., Panizo, F. M., Rodriguez, B. and Valverde, S. (1969) *Tetrahedron Letters* 599.
6. Piozzi, F., Venturella, P., Bellino, A., Paternostro, M. P., Rodriguez, B. and Valverde, S. (1971) *Chem. Ind. (Lond.)* 962.
7. Dennis, D. T., Upper, C. D. and West, C. A. (1965) *Plant Physiol.* **40**, 948.
8. Gonzalez, A. G., Fraga, B. M., Hernandez, M. E. and Luis, J. G. (1973) *Tetrahedron* **29**, 561.
9. Hanson, J. R. and Sarah, F. unpublished results.
10. Hanson, J. R., Hawker, J. and White, A. F. (1972) *J. Chem. Soc. Perkin* 1 1892.

Phytochemistry, 1978, Vol 17, pp 814–815 Pergamon Press Printed in England.

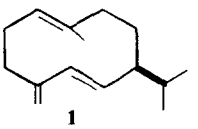
KAURENIC ACID DERIVATIVES FROM *ADENOSTEMMA CAFFRUM*

FERDINAND BOHLMANN und PRANDIP K. MAHANTA
Institute of Organic Chemistry, Technical University Berlin D-1000 Berlin 12, Strasse des 17. Juni 135, W. Germany

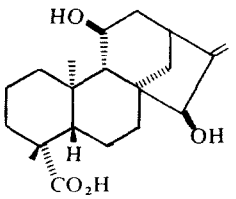
(*Received* 21 *September* 1977)

Key Word Index—*Adenostemma caffrum;* Eupatorieae; Compositae ikaurenic acid derivatives; diterpenoids.

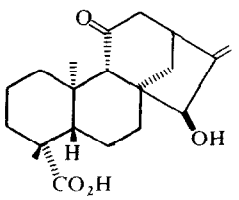
All parts of the South African species *Adenostemma caffrum* DC, contain, besides Germacrene D (**1**) the three kaurenic acid derivatives **2**, **3** and **4** identical with those previously isolated from *Eupatorium album* [1] The only previous investigation of a *Adenstemma* species is a report on isolation of the widespread pentaynene [2]. The co-occurrence of the same diterpenes in a *Eupatorium* änd a *Adenostemma* species indicates a close relationship between these two genera.



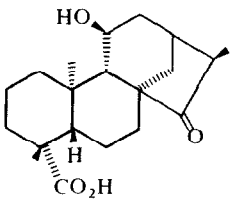
1



2



3



4

EXPERIMENTAL

The air dried plant material (collected in Natal, voucher 77/86) was extracted with Et_2O–petrol (1:2) and the extracts were separated by column chromatography and further by TLC (Si gel GF 254) using Et_2O–petrol mixtures as solvents, 144 g of roots afford 20 mg **1**, 40 mg **2**, 5 mg **4** and 10 mg **3**, while 285 g aerial parts yielded 30 mg **1**, 40 mg **2**, 22 mg **4** and 30 mg **3**. The structures were elucidated by 270 MHz-^{1}H-NMR and by transformation of the acids to methyl esters and by

* Part 130 in the series 'Naturally Occurring Terpene Derivatives'; for part 129 see: Bohlmann, F. and Zdero, C. (1978) *Phytochemistry* **17**, 565.

acetylation and chromic acid/pyridium oxidation of the hydroxyl groups. The spectral data, the mps and the optical rotations of all compounds are in good agreement with those reported in the literature [1].

Acknowledgements—We thank Dr. O. Hilliard, Dept. of Botany, University of Natal, for her help in the identification of the plant material and the 'Deutsche Forschungsgemeinschaft' for supporting this work.

LITERATURE

1. Herz, W. and Sharma, R. P. (1976) *J. Org. Chem.* **41**, 1021.
2. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.

Phytochemistry, 1978, Vol 17, pp 815–817 Pergamon Press. Printed in England

TRITERPENES FROM THE BLED RESIN OF *PISTACIA VERA**

ROMUALDO CAPUTO†, LORENZO MANGONI†, PIETRO MONACO†, GIOVANNI PALUMBO†, YAGHOUB AYNEHCHI‡ and MOUSA BAGHERI‡

†Institute of Organic and Biological Chemistry of the University Via Mezzocannone 16, Napoli 80134, Italy; ‡ School of Pharmacy, University of Tehran, Iran

(*Received* 24 *October* 1977)

Key Word Index—*Pistacia vera*; galls, triterpene composition.

INTRODUCTION

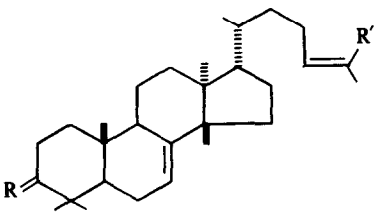
In connection with previous work concerning the chemical study of the galls of plants belonging to the *Pistacia* genus, we have now examined the chemical composition of the oleoresin exuded from the trunk of *P. vera*. Comparative chemical studies of galls and of uninfected tissues of the gall forming plant have not been carried out up to now. To our knowledge, such a comparison has only been reported for *Quercus robur* galls by *Cynips mayri* and this study showed the metabolism in the gall tissues to be greatly altered and leading to triterpenes with different skeletons as well as to increased amounts of highly oxidized substances [2].

RESULTS

The crude oleoresin, collected during Summer, was treated with cold Et_2O to remove polymers and other foreign materials. The light yellow viscous oil thus obtained was subsequently fractionated by conventional methods to give a semicrystalline acid fraction (40%) and an oily neutral fraction (60%).†

The acid fraction, submitted to repeated chromatography on HCl washed Si gel, afforded seven triterpene acids identified as the corresponding methyl esters which are listed in Table 1. All the structures were assigned on spectroscopic grounds and by comparison with authentic samples.

The unknown acetoxy esters (**1b**) and (**2b**) were converted into the corresponding hydroxy methyl esters [5] by alkaline hydrolysis followed by esterification with ethereal diazomethane.



(**1a**) R = O ; R′ = CO_2Me
(**1b**) R = H, αOAc; R′ = CO_2Me
(**1c**) R = H, βOH ; R′ = CO_2Me
(**1d**) R = H, αOH ; R′ = CO_2Me
(**1e**) R = H, βOH ; R′ = CH_2OH
(**1f**) R = O ; R′ = CHO

* Part 6 in the series 'Anacardiaceae'. For Part 5 see ref. [1].
† All the percentages are referred to the ethereal extract.

Table 1. The acidic triterpene methyl esters obtained from *Pistacia vera* resin*

Methyl esters		mp	$[\alpha]_D$	%Amount	Ref.
Masticadienonate	(**1a**)	125–126	−73	8.7	3
3-*O*-Acetyl-3-epimasticadienolate	(**1b**)	129–130	−26	3.5	—
Isomasticadienonate	(**2a**)	110–111	+36	3.4	4
Masticadienolate	(**1c**)	121–123	−43	2.0	5
3-*O*-Acetyl-3-epiisomasticadienolate	(**2b**)	86–87	−2	1.8	—
3-Epimasticadienolate	(**1d**)	100–101	−45	1.1	5
24,25-Dihydromasticadienonate	(**3a**)	91–93	−76	0.9	6
24,25-Dihydro-3-epimasticadienolate	(**3b**)	Oily	—	0.8	†
Oleanonate	(**4a**)	180–182	+76	0.5	7

* Fatty acids and minor components: 12.8%.
† Characterized as the corresponding acid [6] mp 96–97°, $[\alpha]_D$ −47°.