EtOH). The IR spectrum showed strong absorption at 3400–2300, 3070, 1685, 1675, 1635, 1415, 1255 e 895 cm^{-1} suggesting the presence of carboxyl, conjugated double bond and terminal methylene groups; confirmed by the PMR spectrum which showed also signals of three methyl groups. Mono- and dimethyl esters were prepared. Dimethyl agathate [5–7], $[\alpha]_D^{25}$ +54° (*c* 1, $CHCl_3$); MS M^+ *m/e* 348·2293 ($C_{22}H_{34}O_4$), was reduced to agathadiol [5–7], mp 104–106°, $[\alpha]_D^{25}$ +32° (*c* 1, $CHCl_3$). (e) *Agatholic acid* [7] (350 mg), mp 183–184°; $[\alpha]_D^{25}$ +46° (*c* 1, EtOH). The IR spectrum had strong absorption at 3500–2400, 3280, 3075, 1680, 1655, 1250, 1240, 1165, 1040 and 905 cm^{-1}, indicating the presence of carboxyl, hydroxyl, conjugated double bond and terminal methylene groups. The PMR spectrum was similar to that of agathic acid, excepting the AB quartet due to $-C\underline{H}_2OH$. Methyl agatholate [7], mp 71–73°; $[\alpha]_D^{25}$ +43° (*c* 1, $CHCl_3$); MS M^+ *m/e* 334·2502 ($C_{21}H_{34}O_3$), was prepared and reduced to agathadiol. (f) *Imbricatolic acid* [8,9] (0·79 g), oily (mp 52–60°, after drying *in vacuo*); $[\alpha]_D^{25}$ +48° (*c* 1, $CHCl_3$); MS M^+ *m/e* 322. The absorption bands in the IR spectrum at 3400, 3200–2400, 3080, 1700, 1650, 1265 and 890 cm^{-1} suggested the presence of carboxyl, hydroxyl and terminal methylene groups; confirmed by the PMR spectrum δ ($CDCl_3$) 0·55 (*s*, Me at C−10); 0·90 (*br*, Me at C−13); 1·25 (*s*, Me at C−4); 3·60 (*t*, $J \sim 6$Hz, $-CH_2C\underline{H}_2OH$); 4·50 and 4·75 (both *br s*, $=CH_2$) and 7·75 (*br s*, COOH and OH). The acetate (acetyl-imbricatolic acid), $[\alpha]_D^{25}$ +45° (*c* 1, $CHCl_3$), showed in MS, M^+ *m/e* 364·2602 ($C_{22}H_{36}O_4$). The methyl ester of (f), $[\alpha]_D^{25}$ +47° (*c* 1, $CHCl_3$), MS M^+ *m/e* 336, was reduced to imbricatadiol [8,9], mp 111–113°; $[\alpha]_D^{25}$ +25° (*c* 1, $CHCl_3$). Authentic samples were not available but the spectral data were in accordance with those reported for the three diterpenic acids [5–9].

Acknowledgements—The authors are indebted to Dr. Ernest Wenkert, Rice University, Houston, Texas, U.S.A., for providing the high resolution MS, and to the Conselho Nacional de Pesquisas and Fundação de Amparo à Pesquisa do Estado de São Paulo (Brazil), for grants.

REFERENCES

1. Rizzini, C. R. (1971) *Árvores e Madeiras Úteis do Brasil—Manual de Dendrologia* p. 30 Editora da Universidade de São Paulo, São Paulo.
2. Dryselius, E. and Lindberg, B. (1956) *Acta Chem. Scand.* **10**, 445.
3. Lombardi, N., Santamaria, P. M. and Bonino, R. C. D. C. (1970) *Rev. Soc. Quim. Mex.* **11**, 148.
4. Devon, T. K. and Scott, A. I. (1972) *Handbook of Naturally Occurring Compounds*, Vol. II, p. 218. Academic Press, New York.
5. Carman, R. M. and Marty, R. A. (1966) *Austr. J. Chem.* **19**, 2403.
6. Arya, V. P. Erdtman, H. and Kubota, T. (1961) *Tetrahedron* **16**, 255.
7. Enzell, C. (1961) *Acta Chem. Scand.* **15**, 1303.
8. Weismann, G., Bruns, K. and Gruetzmacher, H. Fr. (1965) *Tetrahedron Letters.* **15**, 4623.
9. Bruns, K. and Weismann, G. (1966) *Tetrahedron Letters.* **17**, 1901.

Phytochemistry, 1975, Vol. 14, pp. 2300–2302. Pergamon Press. Printed in England.

TEREBENTHIFOLIC ACID AND BAUERENONE: NEW TRITERPENOID KETONES FROM *SCHINUS TEREBENTHIFOLIUS*

JAYR DE PAIVA CAMPELLO and ANITA J. MARSAIOLI

Instituto de Química, Universidade Estadual de Campinas, C.P. 1170, 13.100 Campinas, São Paulo, Brasil

(*Received* 14 *March* 1975)

Key Word Index—*Schinus terebenthifolius*; Anacardiaceae; amyrin; amyrenone; bauerenone; terebenthifolic acid.

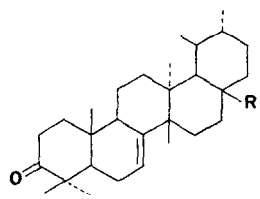
Studies of the terpene constituents of *Schinus terebenthifolius* Radii, commonly known as Aroeira, have led to the isolation of schinol [1–4], masticadienonic acid [3], sitosterol, triacontane, and simiarenol [4]. This note describes the isolation of additional triterpenes and their characterization by chemical and spectral methods. The benzene extract of dried and finely ground bark,

subjected to various chromatographic separations, yielded a series of fractions, listed below in increasing order of polarity. An oily fraction containing two ketones, yielded upon repeated crystallization 50 mg of fine needles. The IR spectrum revealed only one carbonyl group (1710 cm^{-1}), a double bond (1475 cm^{-1}) and a gem-dimethyl group (1380–1390 cm^{-1}). The PMR spectrum of this ketone in $CDCl_3$ suggested the presence of 6 tertiary methyl groups at δ 0·92, 0·99, 1·02, 1·03, 1·03, 1·10; two secondary methyl groups at δ 0·89 and 1·04 each with J values of 5 Hz; and an olefinic hydrogen multiplet at δ 5·43. These facts pointed to a triterpene ketone skeleton, but the clue to its identity came from a close study of its MS which was identical with that of synthetic bauerenone (**1**) [5]. Upon reduction with $LiAlH_4$, the isolated ketone gave a 3β-alcohol having physical properties identical with those of bauerenol, thus confirming the isolation of bauerenone (**1**) as a natural product.

The remaining oily fraction was treated with $LiAlH_4$ and the product crystallized from EtOAc. The MS, IR and PMR spectra showed that the product was a mixture of bauerenol and another triterpene. Upon repeated crystallization from Et_2O–C_5H_5N a small amount of α-amyrin was isolated. These facts indicate the probable presence of baurenone and amyrenone in the original oily fraction.

A solid fraction containing two triterpenes, was also obtained. As TLC, column chromatography and repeated crystallization were not effective for their separation, the mixture was acetylated and then subjected to chromatography on alumina–$AgNO_3$. The main compound obtained was identical in all respects with an authentic sample of α-amyrin acetate, suggesting the presence of α-amyrin in the original mixture.

In our previous work [4] we had mentioned the isolation of a triterpenic acid, $C_{30}H_{46}O_3$, terebenthifolic acid; and we now propose its structure as based on spectral data. The IR spectrum showed absorption bands of carboxy, carbonyl, gem-dimethyl and double bond units. Its PMR spectrum in $CDCl_3$ revealed 5 tertiary methyl group singlets at δ 0·88, 1·04, 1·10, 1·25, 1·25; two secondary methyl groups doublets at δ 1·00 and 1·05 with J value of 5 Hz; and an olefinic hydrogen multiplet at δ 5·30. The UV spectrum was



(**1**) R = Me
(**2**) R = CO_2H

characteristic of a non-conjugated carbonyl moiety. A close study of its MS revealed a great similarity to that of bauerenone [5], except for an ion of m/e 235. This was explained by comparison with the fragment at m/e 205 from bauerenone, which consists of rings E. D and the C_{28} methyl group. The difference of 30 amu was attributed to the change from the methyl (bauerenone) to a carboxy group at C_{28}. Based on the above spectral evidence we propose the structure of terebenthifolic acid as baueren-28-carboxy-3-one. Unfortunately there was insufficient material for further analysis.

From the phytochemical study of the leaves and bark of *Schinus terebenthifolius*, it became evident that the compounds obtained show a greater similarity to compounds isolated from *Pistacia* [6–8] species, than with those isolated from other species of *Schinus*.

EXPERIMENTAL

Mp's were determined on a Reichert micro hot stage and are uncorrected. PMR spectra in $CDCl_3$ with internal TMS, were taken on Varian A-60, HA-100, HA-220 spectrometers. MS were determined in the direct inlet system of an AEI MS-9, Varian CH-7, C.E.-21-110 or Finnigan S/L 1015. Column chromatography was performed on 70–230 mesh silica and TLC on Merck Si gel. The material was collected in April in the vicinity of Curitiba, State of Paraná, Brazil.

Extraction. 183 g of crude bark extract (3·7% of the dried bark) was chromatographed on a 1 kg Si gel column and eluted with solvents of increasing polarity (from hexane to C_6H_6 and EtOAc–EtOAc) collecting 500 ml fractions.

Bauerenone. Eluted with hexane–C_6H_6 3:1, was crystallized from EtOAc, yielding 50 mg of fine needles; mp 240°, $[\alpha]_D^{25}$ −47·5 (*c*, 1, $CHCl_3$); IR ν_{max}^{KBr} (cm^{-1}) 3050 (–C=C), 2950 and 2870 (–Me, $-CH_2$), 1710 (–C=O), 1380 and 1390 (–C–$(Me)_2$); PMR δ 0·89 (*d*, J 6 Hz, –CH–C$\underline{H}_3$), 0·92 (*s*, –Me), 0·99 (*s*, –Me), 1·02 (*s*, –Me), 1·03 (*s*, 2–Me), 1·04 (*d*, J 6 Hz, –CH–C$\underline{H}_3$), 1·10 (*s*, –Me), 2·74 (sex., J 6 and 14 Hz, –CO–C$\underline{H}$), 5·43 (*m*, $\underline{H}$–C=C–); M^+ at m/e 424·7012 (13%) (calc for $C_{30}H_{48}O$, 424·7164); C_xH_yO m/e (%); $C_{29}H_{45}O$, 409·3505 (11), $C_{19}H_{28}O$, 271·2046 (13), $C_{18}H_{25}O$, 257·1902 (17), $C_{17}H_{25}O$, 245·1912 (100), $C_{15}H_{22}O$, 218·1653 (12), $C_{15}H_{25}$, 205·1978 (22).

Reduction of bauerenone. Bauerenone (13·6 mg) in dry Et_2O, was reduced with LAH (15·0 mg) under refluxed for 3 hr. The product was crystallized from Et_2O–MeOH, mp 199–204°; $[\alpha]_D^{25}$ −36 (*c*, 0·5, $CHCl_3$); M^+ at m/e 426.

α-Amyrenone reduction. The bauerenone mother liquor consisted of an oily fraction containing two triterpenic ketones. As the usual crystallization methods were not effective, the

mixture (2 g) was reduced with LAH (1 g) in Et_2O and the product, after repeated crystallization from pyridine–Et_2O, yielded an alcohol (0·19 g), mp 180–182; $[\alpha]_D^{25}$ +80 (*c*, 2, $CHCl_3$); M^+ at *m/e* 426.

α-Amyrin. Eluted with hexane–C_6H_6 (3:1) as a mixture of 2 triterpenes (5 g) which could not be separated by column chromatography or TLC. The mixture was acetylated (pyridine–Ac_2O) 1:1 at room temp. for 24 h. The product was crystallized from C_5H_5N–Et_2O; 50 mg of the acetates were treated with freshly sublimed SeO_2 (100 mg) and HOAc (2 ml). After 6 hr reflux the product was purified on an alumina–$AgNO_3$ column and eluted, with $CHCl_3$, yielding 5 mg of α-amyrin acetate. M^+ at *m/e* 468; mp 219–220°; $[\alpha]_D^{25}$ +80 (*c*, 2, $CHCl_3$).

Terebenthifolic acid. The acidic fraction of the benzene extract of the leaves, eluted from a silica column with hexane–Et_2O (1:1) yielded (61 mg) of fine needles, mp 270°; IR ν_{max}^{KBr} (cm^{-1}) 3500–2500 (–CO<u>OH</u>), 1700 (–C=O conj), 1710 (–<u>C</u>=O), 1380 and 1370 (–C–Me_2); UV λ_{max}^{MeOH} 210 nm, ϵ_{max} 25; PMR δ 0·88 (*s*, –Me), 1·00 (*d*, *J* 5 Hz, –CH–<u>CH</u>$_3$), 1·04 (*s*, –Me), 1·05 (*d*, *J* 5 Hz, –CH–<u>CH</u>$_3$), 1·11 (*s*, –Me), 1·25 (*s*, 2–Me), 2·74 (*m*, –CO–<u>CH</u>), 5·30 (*m*, –C=<u>C</u>–<u>H</u>). M^+ at *m/e* (%) 454·3485 (48) (calc. for $C_{30}H_{46}O_3$: 454·3447); C,H,O *m/e* (%), $C_{29}H_{43}O_3$, 439·3212 (52); $C_{19}H_{28}O$, 272·2186 (5), $C_{18}H_{25}O$, 257·1948 (21), $C_{17}H_{25}O$, 245·1941 (100), $C_{15}H_{23}O_2$, 235·1721 (65), $C_{15}H_{22}O$, 218·1666 (12).

Acknowledgements—The authors are indebted to Professor Ernest Wenkert, Indiana University, Bloomington, Indiana, U.S.A., for providing MS and NMR spectra; to Professor Ralph J. G. Hertel, Faculdade de Filosofia, Ciências e Letras da Universidade Federal do Paraná, Brazil, for assistance in collection, and identification of the plant and to the Fundação de Amparo à Pesquisa do Estado de São Paulo and the Conselho Nacional de Pesquisas (Brazil), for grants.

REFERENCES

1. Kaistha, K. K. and Kier, L. B. (1962) *J. Pharm. Sci.* **51**, 245.
2. Kaistha, K. K. and Kier, L. B. (1962) *J. Pharm. Sci.* **51**, 1136.
3. Kier, K. K., Lehn, J. M. and Ourisson, Y. (1963) *Bull. Soc. Chim. Fr.* 911.
4. Campello, J. P. and Marsaioli, A. J. (1974) *Phytochemistry* **13**, 659.
5. Budzikiewicz, H., Wilson, J. M. and Djerassi, C. (1963) *J. Am. Chem. Soc.* **85**, 3688.
6. Barton, R. H. R. and Seone, E. (1956) *J. Pharm. Sci.* 4150.
7. Seone, E. (1959) *J. Chem. Soc.* 4158.
8. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1973) *Phytochemistry* **12**, 939.

Phytochemistry, 1975, Vol. 14, pp. 2302 2303. Pergamon Press. Printed in England.

A NEW LIGNAN FROM *CARISSA CARANDAS**

RAGHWENDRA PAL, D. K. KULSHRESHTHA and R. P. RASTOGI

Central Drug Research Institute, Lucknow, India

(*Received* 7 *March* 1975)

Key Word Index—*Carissa carandas*; Apocynaceae; lignan; carinol; demethyltetrahydrogmelinol.

The alcoholic extract of the roots of *Carissa carandas* L. has been reported to possess cardiotonic activity [1] and to produce a perceptible decrease in blood pressure in normal anaesthetized cats [2]. Chemical studies have led to the isolation of possibly a new cardioactive substance [3]; glucosides of odoroside H [4], a new terpenoid carindone [5] besides carissone, lupeol, ursolic acid and its methyl ester [6]. A recent investigation of the pharmacological activity [7] of the extract showed an increase in free histamine in the guinea pig lung and a pronounced decrease in blood pressure at 1 mg/kg dose which lasted for 4–5 hr. On fractionation of the extract, the hypotensive activity was found to be localized in the C_6H_6-soluble fraction which prompted further examination of its constituents.

The active fraction was fractionated into Et_2O and $CHCl_3$ soluble and insoluble fractions and the activity was now found to be present in the $CHCl_3$-insoluble fraction. It showed one major spot R_f 0·38 in $CHCl_3$–EtOAc (1:4) (TLC), and was chromatographed over Si gel which led to the isolation of the substance corresponding to the above spot as an amorphous powder, named "carinol". The $CHCl_3$–MeOH (98:2) eluates containing carinol were found to be inactive whereas the subsequent eluates which possessed hypoten-

* CDRI Communication No. 2024.