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).

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A NEW LIGNAN FROM *CARISSA CARANDAS**

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

Central Drug Research Institute, Lucknow, India

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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-

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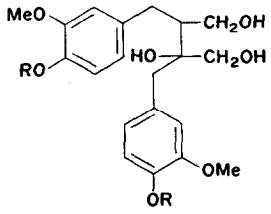
sive activity, showed only streaking and no pure substance has so far been isolated.

Carinol, $C_{20}H_{26}O_7$ (M^+ 378), was a phenolic lignan and showed characteristic IR peaks for hydroxyl (3300) and trisubstituted benzene ring (1600, 1529, 1157, 1054, 1027, 831 and 800 cm^{-1}). The PMR spectrum of carinol exhibited two benzylic methylenes at 2·50 (*m*) and 2·88 (*s*), two $-CH_2-O-$ groups at 3·70 (*s*) and 3·81 (*d*, *J* 4 Hz), two aromatic methoxyls at 3·90 and six aromatic protons in the region of 6·65–7·10 ppm.

Structure (**1**) was deduced for carinol, from the results of periodate oxidation and from spectral analyses of the compound itself and of its tetracetate, dimethyl ether and dimethyl ether diacetate (see Experimental). This structure was confirmed by the identity of its dimethyl ether (**2**) with tetrahydrogmelinol (mp 131°, $(\alpha)_D$, −3·0°), the Birch reduction product of gmelinol [8].



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

EXPERIMENTAL

Carinol. amorphous powder, $(\alpha)_D$ −22·4° (C 1·0, EtOH). It gave a green colour with ferric chloride; ν_{max}^{KBr}: 3300 (OH), 2910 (CH_2), 1600, 1529, 1157, 1054, 1027 and 800 cm^{-1} (aromatic). λ_{max}^{EtOH}: 215, 230 and 281 nm (ε 9000, 11840 and 5620); λ_{max}^{NaOH}: 248 and 296 nm (ε 16250 and 6400), PMR (Acetone "d_6"): ppm 2·50 (2 H, *m*, Ph–C<u>H</u>$_2$–CH–), 2·88 (2 H, *s*, Ph–CH_2–), 3·70 (2 H, *s*, –O–CH_2–), 3·81 (2 H, *d*, *J* 4 Hz, –O–CH_2–), 3·90 (6 H, *s*, 2–OMe), 6·65–7·10 (6 ArH). MS: *m/e* 378 (M^+), 360, 329 (M–H_2O–CH_2OH), 240, 223, 219, 205, 175, 137 (Ph (OH, OMe) CH_2) (base peak) and 122. Found: C, 58·64; H, 7·62 $C_{20}H_{26}O_7$ requires C, 58·42; H, 6·82%.

The tetraacetate. crystallized from C_6H_6–C_6H_{14}, mp 118°, $(\alpha)_D$ +6·4° (C, 1, EtOH). ν_{max}^{KBr}: 3401 (OH), 2907 (CH_2), 1773 and 1742 (phenolic and aliphatic acetate respectively). 1600, 1506, 1144, 1106, 1027, 906 and 801 cm^{-1} (aromatic). λ_{max}^{EtOH}: 225, 273, 278 and 296 nm (ε 13250, 5076, 4240 and 9170) which shifted to 249 and 290 nm (ε 17652 and 8250) on addition of a drop of 10% NaOH. PMR: ppm 2·00, 2·09 (3 H each, *s*, 2 –OCOMe), 2·30 (6 H, *s*, 2 –OCOMe), 2·60 (2 H, *m*, Ph–C<u>H</u>$_2$–CH–) 2·97 (2 H, *s*, Ph–CH_2), 3·86 (6 H, *s*, 2 OCMe), 4·18 (2 H, *brd s*, –CH_2–OAc), 4·29 (2 H, *d*, *J* 5 Hz –C<u>H</u>$_2$OAc), 6·80–6·98 (6 ArH). MS: *m/e* 546 (M^+), 504 (M –CH_2=C=O), 367 (M –CH_2=C=O– 137), 324, 289, 247, 205, 180, 163 and 137. Found: C, 61·25; H, 6·51. $C_{28}H_{34}O_{11}$ requires C, 61·77; H, 6·28%.

Carinol dimethyl ether. crystallized from $CHCl_3$, mp 130–1°, $(\alpha)_D$ −3·0° (C, 1·0, EtOH) ν_{max}^{KBr}: 3401, 2907, 1600, 1517, 1157 and 800 cm^{-1}, λ_{max}^{EtOH}: 230, 280 and 292 nm, PMR (Acetone "d_6"): ppm 2·60 (2 H, *m*, Ph–C<u>H</u>$_2$–CH–), 2·80 (3 H, *brd s*, D_2O exchangeable), 2·93 (2 H, *s*, Ph–C<u>H</u>$_2$–), 3·55 (2 H, *s*, –OCH_2–), 3·73 (2 H, *d*, *J* 4 Hz –OCH_2–), 3·83 (12 H, *s*, 4 OMe), 6·88–7·10 ppm (6 ArH). MS: *m/e* 406 (M^+), 388, 357 (M–H_2O–CH_2OH), 254, 237, 219, 189, 160 and 151 [$Ph(OMe)_2CH_2$] (base peak).

Carinol dimethyl ether diacetate was obtained as an amorphous powder, R_f 0·40 in $CHCl_3$ (TLC) ν_{max}^{KBr}: 3401 (OH), 3125 and 2865 (CH_2), 1742 and 1252 (OAc), 1600, 1144, 1027 and 817 cm^{-1}. PMR: ppm 2·01 and 2·10 (3 H each, *s*, 2 –OCOMe), 2·60 (2 H, *m*, Ph–C<u>H</u>$_2$–CH–), 3·00 (2 H, *s*, Ph–C<u>H</u>$_2$–), 3·96 (12 H, *s*, 4 –OMe), 4·17 (2 H, *s*, –C<u>H</u>$_2$OAc), 4·31 (2 H, *d* 4 Hz, –C<u>H</u>$_2$–OAc), 6·80–6·95 ppm (6 ArH). PMR with TAI: ppm 8·50 (1 H, *brd s*, –CO–NH–CO–), MS: *m/e* 490 (M^+), 339 (M-151), 261 (M –H_2O–MeCOOH– 151), 219 (M –H_2O–CH_2=C=O– 151) and 151.

Sodium periodate oxidation of carinol. Carinol (100 mg) in EtoAc–EtOH (1:3, 2 ml) and aqueous $NaIO_4$ (0·5 ml, 62 mg) were kept for 24 hr at room temp. The reaction mixture was chromatographed over Si gel when $CHCl_3$–EtOAc (1:1) eluate yielded the product (R_f 0·36 $CHCl_3$–EtOAc, 1:2), 22 mg, as amorphous powder. ν_{max}^{KBr}: 3340 (OH), 2950 (CH_2), 1698 (–C=O), 1600, 1259, 1151 and 800 cm^{-1}. PMR: ppm 2·70 (2 H, *m*, Ph–C<u>H</u>$_2$–), 3·14 (1 H, *m*, –CO–CH–), 3·52 (2 H, *s*, Ph–C<u>H</u>$_2$–), 3·76 (2 H, *d*, *J* 4 Hz, –O–CH_2–), 3·82 (6 H, *s*, 2 –OMe), 6·50–6·95 (6 ArH). MS: *m/e* 346 (M^+), 328, 316, 297 (M –H_2O–CH_2OH), 209 (M-137), 191 (M–H_2O–137) and 137. Its acetyl derivative and R_f 0·52 in $CHCl_3$–EtOAc (1:1), ν_{max}^{KBr}: 2994, 2907 (CH_2), 1773 (phenolic acetate), 1737 (aliphatic acetate), 1700 (–C=O). PMR: ppm 2·00 (3 H, *s*, OAc), 2·31 (6 H, *s*, 2-OAc), 2·78 (2 H, *m*, Ph–C<u>H</u>$_2$), 3·20 (1 H, *m*, –CO–CH–), 3·51 (2 H, *s*, Ph–CH_2–), 3·76 and 3·78 (3 H each, *s*, 2 –OMe), 4·23 (2 H, *d*, *J* 6 Hz, –C<u>H</u>$_2$OAc), 6·66–7·03 (6 ArH). MS: *m/e* 472 (M^+), 430, 370 (M–CH_2=C=O–MeCOOH), 328 [M–2(CH_2=C=O)–MeCOOH], 191 (M–2(CH_2=C=O)–MeCOOH–137) and 137.

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