Monatshefte für Chemie 121, 941 – 944 (1990)

Monatshefte für Chemie
Chemical Monthly

Natural Product Chemistry, Part 100 [1]: The Structure of Carissone, $C_{15}H_{24}O_2$

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Summary. $C_{15}H_{24}O_2$, $M = 236.2$, monoclinic, $P2_1$, $a = 7.229\,(7)$, $b = 14.925\,(9)$, $c = 6.235\,(9)$ Å, $\beta = 92.40\,(9)°$, $V = 672.1$ Å^3, $T = -133$ °C, $Z = 2$, $D_x = 1.17$ g cm^{-3}. The X-ray diffraction analysis of this sesquiterpenoid from *Carissa opaca* confirmed the previously proposed constitution of the isolate and, furthermore, allowed precise NMR assignment.

Keywords. *Carissa opaca*; Carissone; X-ray diffraction analysis; Sesquiterpenoid.

Naturstoffchemie, 100. Mitt.: Die Struktur des Carissons, $C_{15}H_{24}O_2$

Zusammenfassung. $C_{15}H_{24}O_2$, $M = 236.2$, monoklin, $P2_1$, $a = 7.229\,(7)$, $b = 14.925\,(9)$, $c = 6.235\,(9)$ Å, $\beta = 92.40\,(9)°$, $V = 672.1$ Å^3, $T = -133$ °C, $Z = 2$, $D_x = 1.17$ g cm^{-3}. Die Röntgenstrukturanalyse dieses Sesquiterpenoids aus *Carissa opaca* bestätigte die bereits vorgeschlagene Struktur und erlaubte ferner eine genaue NMR-Zuordnung.

Introduction

The eudesmol type sesquiterpene Carisson, $C_{15}H_{24}O_2$ (4,4a,5,6,7,8-hexahydro-7-(1-hydroxy-1-methylethyl)-1,4a-dimethyl-2(3*H*)-naphthalenone(4a *S-cis*) was isolated form *Carissa lanceolata* root (Family Apocynaceae) [2]. Later on, this compound was found in other investigated members of the genus [3] and its synthesis has been documented [4]. We now report the isolation of carissone from the root of *C. opaca* Stapf. ex R. N. Parker. This species grows in the dry northern regions of India [1], where it is an important constituent of the semi-arid scrubland vegetation [5]. Its ground roots is used as a component of purgatives, an antidote to snakebite and applied to worm-infested sores of animals [6, 7]. Some carissone-related sesquiterpenes have been considered as phytoalexins possessing antifungal activity [8].

[1] The name *C. spiranum* A. DC. has been frequently misapplied in literature; Lucas H. L., Kew Gardens, Richmond, England; personal communications

Experimental

Crystallization occurred from a *n*-hexane–dichloromethane solution; Colorless crystals, 0.24 × 0.20 × 0.16 mm; Synthex $P2_1$ diffractometer, $2\theta/\theta$ mode, scan speed 4–30 deg min^{-1}, graphite monochromated MoKα radiation; 1 530 low-temperature reflections measured ($4 < 2\theta < 54°$), of which 1 352 with $I > 2\sigma(I)$. For structure analysis and refinement direct methods (MULTAN) were used, C and O atoms from $E-$ map, H coordinates from $\Delta F-$ map. Full matrix least-squares refinements with all nonhydrogen atoms anisotropic and hydrogens with fixed coordinates and isotropic U (0.06 Å^2). The weighting scheme $w^{-1} = [\sigma(F_o)^2 + (0.006|F_o|)$ with $\sigma(F_o) = \sigma(I)/(2|F_o|L_p)$ gave satisfactory agreement analysis. Final R and R_w values are 0.052 and 0.053 with 153 variables, calculations were done with SYNTEX XTL system.

Results and Discussion

Isolation and Characteristics of Carissone

An aqueous methanol extract of the powdered root was partitioned with toluene and the toluene fraction was chromatographed on a silica gel column packed with toluene. Eluation was affected with toluene-ethyl acetate mixtures, this furnished carissone in a 0.7% *w/w* yield.

The isolate showed m.p., $[\alpha]_D$, UV, IR, and MS data similar to those previously published for carissone [2, 4]). ^{1}H NMR ($CDCl_3$ 300 MHz): δ (ppm) = 2.72 (1 H, m, J = 13.7, 3.9, 1.8 Hz, 3-H), 2.34 (2 H, m, J = 11.0, 5.5, 1.4 Hz, 10-H, 11-H), 1.95 (3 H, d, J = 1.5, 15-CH_3), 1.68 (1 H, m, J = 13.7, 12.2, 1.5, 1.2 Hz, 4-H), 1.01 and 1.00 (6 H, 2 s, 12- and 13-CH_3), 0.84 (3 H, s, 14-CH_3). ^{13}C NMR (75.4 MHz, C_6D_6): δ (ppm) = 198.1 (C-2), 162.7 (C-10), 128.8 (C-1), 71.6 (C-11), 49.9 (C-8), 42.2 (C-4), 37.5 (C-6), 35.9 (C-5), 34.0 (C-3), 29.0 (C-9), 27.8 (C-13), 26.6 (C-12), 22.9 (C-7), 22.3 (C-15), 11.1 (C-14).

Table 1. Atomic coordinates and equivalent isotropic thermal parameters. $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

	x	y	z	U_{eq} (Å^2)
C(1)	0.0013(5)	0.6925(3)	−0.0011(6)	0.020(1)
C(2)	0.1524(5)	0.7539(3)	−0.0552(6)	0.025(1)
C(3)	0.1359(5)	0.8504(3)	0.0095(6)	0.028(1)
C(4)	0.0487(5)	0.8579(3)	0.2280(6)	0.024(1)
C(5)	0.8588(5)	0.8127(3)	0.2295(6)	0.019(1)
C(6)	0.8100(5)	0.8018(3)	0.4690(6)	0.024(1)
C(7)	0.6420(5)	0.7440(3)	0.5061(6)	0.026(1)
C(8)	0.6723(5)	0.6507	0.4146(6)	0.019(1)
C(9)	0.7009(5)	0.6607(3)	0.1702(5)	0.021(1)
C(10)	0.8637(5)	0.7200(3)	0.1258(5)	0.019(1)
C(11)	0.5223(5)	0.5810(3)	0.4647(5)	0.021(1)
C(12)	0.5817(6)	0.4878(3)	0.3998(7)	0.031(1)
C(13)	0.0487(5)	0.8579(3)	0.2280(6)	0.030(1)
C(14)	0.0077(5)	0.5997(3)	−0.0962(6)	0.027(1)
C(15)	0.7120(6)	0.8703(3)	0.1091(7)	0.027(1)
O(1)	0.2863(4)	0.7282(3)	−0.1520(5)	0.033(1)
O(2)	0.5117(4)	0.5757(2)	0.6967(4)	0.029(1)

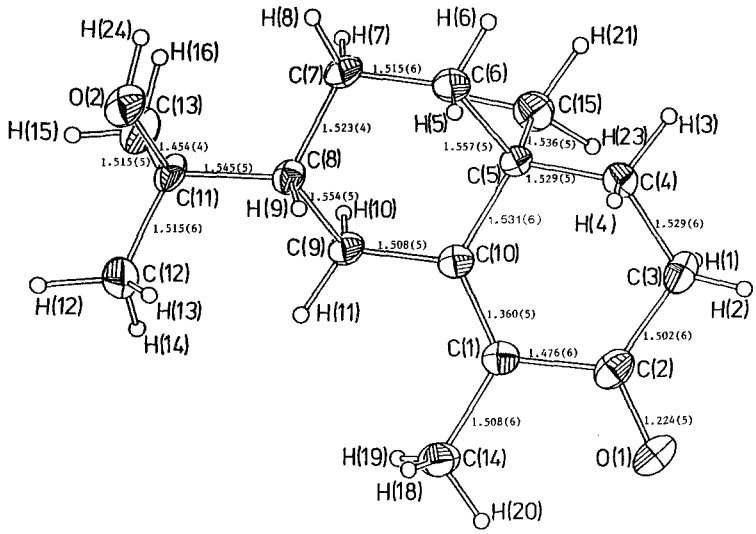

Fig. 1. Structural formula, numbering scheme and bond distances (Å) for the nonhydrogen atoms

Table 2. Selected torsional angles (°) and bond angles (°)

H(1)–C(3)–C(4)–H(3)	−67.3
H(2)–C(3)–C(4)–H(3)	54.6
H(2)–C(3)–C(4)–H(4)	−55.3
H(5)–C(6)–C(7)–H(7)	177.1
H(5)–C(6)–C(7)–H(8)	64.8
H(6)–C(6)–C(7)–H(7)	58.0
H(6)–C(6)–C(7)–H(8)	−54.3
H(9)–C(8)–C(9)–H(10)	174.0
H(9)–C(8)–C(9)–H(11)	69.2
C(2)–C(1)–C(10)	120.8(4)
C(2)–C(1)–C(14)	122.8(4)
C(10)–C(1)–C(14)	116.4(3)
C(2)–C(3)–C(4)	110.5(3)
C(3)–C(4)–C(5)	112.2(3)
C(4)–C(5)–C(6)	106.9(3)
C(4)–C(5)–C(10)	111.1(3)
C(4)–C(5)–C(15)	109.1(3)
C(6)–C(5)–C(10)	108.7(3)
C(6)–C(5)–C(15)	110.3(3)
C(10)–C(5)–C(15)	110.6(3)
C(5)–C(6)–C(7)	114.9(3)
C(7)–C(8)–C(9)	107.9(3)
C(7)–C(8)–C(11)	112.7(3)
C(9)–C(8)–C(11)	115.2(3)
C(8)–C(9)–C(10)	111.9(3)
C(9)–C(10)–C(1)	121.6(3)
C(9)–C(10)–C(5)	115.0(3)
C(1)–C(10)–C(5)	123.4(3)
C(8)–C(11)–O(2)	107.7(3)
C(12)–C(11)–O(2)	104.1(3)
C(13)–C(11)–O(2)	109.2(3)

Crystal Structure

The crystal structure of carissone was determined from single crystal X-ray diffraction data and was refined to a value of 5.2%. Final atomic coordinates within the unit cell and equivalent isotropic thermal parameters are listed in Table 1; an ellipsoid plot of the molecule with the numbering scheme and bond lengths of the nonhydrogen atoms are shown in Fig. 1. Table 2 displays selected torsion angles and bond angles.

The chemical structure of carissone as defined by the X-ray crystallographic results corresponds to 4,4a,5,6,7,8-hexahydro-7-(1-hydroxy-1-methylethyl)-1,4a-dimethyl-2(3*H*)-naphthalenone, thus confirming the previously proposed structure [2].

Acknowledgements

We would like to acknowledge the financial support of the "Deutsche Forschungsgemeinschaft" and the "Heinrich-Hertz-Stiftung".

References

[1] For Part 99 see: Adesina S. K., Reisch J. (1985) Phytochemistry **24**: 3003
[2] Mohr K., Schindler O., Reichstein T. (1954) Helv. Chim. Acta **37**: 462
[3] Achenbach H., Waibel R., Addae-Mensah I. (1983) Phytochemistry **22**: 749
[4] Kutney J. P., Singh A. K. (1982) Can. J. Chem. **60**: 1842
[5] Rao I. M., Swamy P. M., Das V. S. R. (1980) Z. Pflanzenphysiol. **99**: 69
[6] Chopra R. N., Nayar S. L., Chopa I. C. (1956) Glossary of Indian Medicinal Plants. C.S.I.R., New Delhi, India, p. 52
[7] Pakrashi S. C., Datta S., Ghosh-Dastidar P. P. (1968) Phytochemistry **7**: 495
[8] Ward E. W. B., Unwin C. H., Hill J., Stoessl A. (1975) Phytopathol. **65**: 859

Received May 16, 1990. Accepted May 30, 1990