Journal of

The Chemical Society,

Chemical Communications

NUMBER 15/1979 2 AUGUST

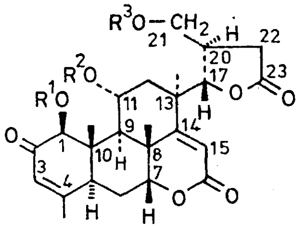
Isolation and Structure (*X*-Ray Analysis) of a New C_{25} Quassinoid Soulameolide from *Soulamea tomentosa*[1]

By Judith Polonsky,* Mai Van Tri, Thierry Prangé, and Claudine Pascard
(*Institut de Chimie des Substances Naturelles, CNRS,* 91190 *Gif sur Yvette, France*)
and Thierry Sevenet
(*Laboratoire des Plantes Médicinales, CNRS, P.O. Box* 1264, *Nouméa, Nouvelle-Calédonie*)

Summary The structure of soulameolide, a novel C_{25} quassinoid isolated from the leaves of *Soulamea tomentosa* (Brongn. and Gris), has been established from spectral data and by single-crystal *X*-ray analysis; the previously known picrasin B, 6-hydroxypicrasin B, and iso-brucein A were also isolated.

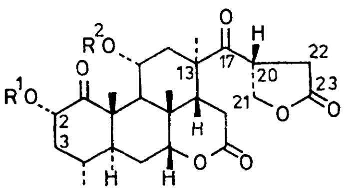
Part of our earlier studies, directed at uncovering new quassinoids[2] produced by Simaroubaceae, was concerned with the New-Caledonian species *Soulamea tomentosa* Brongn. and Gris. Initially 6-hydroxypicrasin B[3,4,5] and iso-brucein A[5] were isolated from the trunk bark. We now report the structural elucidation of a novel quassinoid, soulameolide (**1a**), isolated from the *Soulamea t.* leaf extract. By far the greatest majority of the numerous quassinoids known have a C_{20} basic skeleton. Soulameolide is the third C_{25} quassinoid isolated to date, the two others being simarolide (**2a**)[6] and picrasin A (**2b**).[7] It is also the first example of a natural quassinoid to have a Δ^{14} double bond.

The dried ground leaves (275 g) of *Soulamea tomentosa* were extracted with hexane and several times with hot water. The concentrated aqueous extract was continuously extracted with chloroform. Column chromatography of the chloroform residue (3·1 g) on silica gel and elution with chloroform containing 2% methanol afforded the previously isolated picrasin B[3,7] and iso-brucein A.[5] On increasing to 5% methanol, 6-hydroxypicrasin B[3,4] and soulameolide (**1a**) (0·08 g) were eluted. Purification of the latter was achieved by preparative t.l.c. (ethyl acetate–methanol, 90:10).



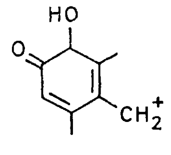
(1)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = H$; $R^2 = R^3 = Ac$
c; $R^1 = Ac$; $R^2 = H$; $R^3 = Ac$

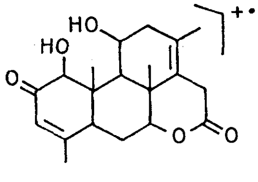


(2)

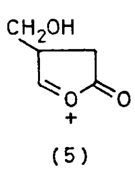
a; $R^1 = H$; $R^2 = Ac$
b; $R^1 = Me$; $R^2 = H$; 2,3 dehydro



(3)



(4)



(5)

The molecular formula of (**1a**) was found to be $C_{25}H_{32}O_6$, *m/e* 460·2117 (M^+); m.p. 261—263 °C; $[\alpha]_D^{22}$ −72·6° (*c* 0·7, MeOH–$CHCl_3$, 2:1). The i.r. spectrum (Nujol) showed three carbonyl bands at 1778 (γ-lactone), 1720 (δ-lactone), and 1680 cm^{-1} ($\alpha\beta$-unsaturated ketone), and, in agreement with the formulation of ring A as in (**1a**), the u.v. spectrum showed a maximum at 238 nm (ϵ 12450), the 250 MHz ^1H

n.m.r. spectrum ($CDCl_3$–pyridine, 9:1) displayed the characteristic signals due to the vinyl methyl, 1-H, and 3-H (δ 1·91, 4·09, and 6·05, respectively) and the mass spectrum showed a peak at *m/e* 151·0765 ($C_9H_{11}O_2$) (**3**).[2] The ^1H n.m.r. spectrum also revealed singlets due to three additional methyl groups at δ 0·92 1·25, and 1·43, and a sharp, downfield, one-proton singlet at δ 6·13 assigned to 15-H. Extensive double resonance experiments identified other signals due to protons on oxygen-bearing carbons: δ 3·70 (2H, octet, 21-H, *J* 11·4, 6·0 Hz which collapses on irradiation at δ 2·62 to an AB quartet), 4·18 (1H, br.s, 7-H), 4·44 (1H, t-like, 11-H, *J* 5·7 Hz), and 4·57 (1H, d, 17-H, *J* 2·2 Hz). These assignments were substantiated by the 250 MHz ^1H n.m.r. spectra of the 11,21-diacetate (**1b**) and the 1,21-diacetate (**1c**), $C_{29}H_{36}O_{10}$, (M^+ at *m/e* 544), obtained by acetylation of (**1a**) with acetic anhydride in pyridine. The ^1H n.m.r. spectra ($CDCl_3$) of both derivatives revealed a significant downfield shift for the 21-H resonance (2H, m, δ 4·15); the 11-H of (**1b**) and the 1-H of (**1c**) were considerably de-shielded and appeared at δ 5·55 (1H, t) and at δ 5·30 (1H, s), respectively.

Structure (**1a**) for soulameolide was further supported by the presence of the base peak at *m/e* 346·1781 ($C_{20}H_{26}O_5$) in its mass spectrum assigned to the fragment ion (**4**) arising by a McLafferty type rearrangement involving the 14,15 double bond and resulting in the cleavage of the 13,17 carbon bond; a weak peak at *m/e* 115·0398 ($C_5H_7O_3$) corresponding to the ion (**5**) was also observed.

Unequivocal proof for the structure and relative stereochemistry of soulameolide (**1a**) was provided by single-crystal *X*-ray analysis. Crystals of (**1a**) were obtained from acetone: orthorhombic, space group $P2_12_12_1$ ($Z = 4$), $a = 11{\cdot}019(4)$, $b = 14{\cdot}238(5)$, and $c = 14{\cdot}694(5)$ Å. 2329 ($1746 \geqslant 2\sigma$) independent reflections were scanned on a four-circle automatic Philips PW 1100 diffractometer using graphite-monochromatised Mo-K_α radiation. The structure was solved by direct methods with the aid of the multi-solution technique,[8] and anisotropically refined to a final conventional *R* factor = 5·1%. (H atoms were kept isotropic and not refined in the last steps.) A view of the molecular conformation is shown in the Figure.†

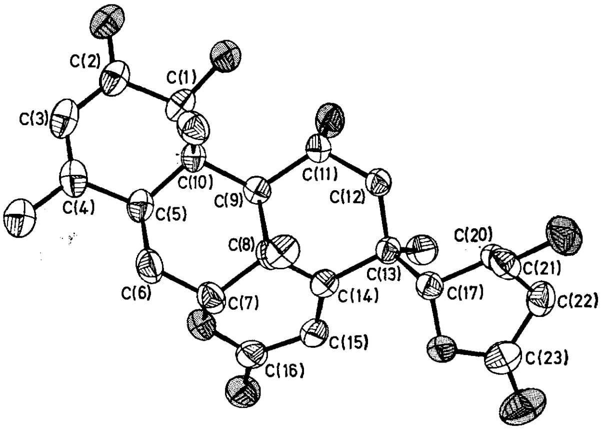


FIGURE. Molecular structure of soulameolide (dotted ellipsoids denote oxygen atoms).

The absolute configuration of soulameolide, also represented in (**1a**), the same as that of simarolide,[6b] follows from the experimentally proven triterpenoid biogenetic origin of the quassinoids.[2]

In soulameolide the 17-CHOH of the triterpenoid biogenetic precursor is involved in the formation of the γ-lactone whereas in simarolide it is the 21-CH_2OH which is engaged in the γ-lactone. The 20-*R* configuration of soulameolide (without an adjacent carbonyl function) suggests that the quassinoids derive from tirucallol rather than from euphol. The presence of the 14,15 double bond in soulameolide also suggests that the oxygenated functions at these carbon atoms, present in several quassinoids, are introduced subsequent to the formation of the δ-lactone.

We thank Ch. Marazano and J. P. Cosson for high resolution mass spectra and M. C. Merienne (Laboratoire de R.M.N. à Haut Champs, Orsay) for ^1H n.m.r. measurements at 250 MHz.

(*Received*, 18*th April* 1979; *Com.* 408.
)

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] For previous paper in this series see J. Polonsky, Z. Varon and E. Soler, *Compt. rend.* (*C*), 1978, **288**, 269.
[2] J. Polonsky, *Fortschr. Chem. Org. Naturstoffe*, 1973, **30**, 101.
[3] B. Viala and J. Polonsky, *Compt. rend.*, 1970, **271**, 410.
[4] C. Pascard, T. Prangé, and J. Polonsky, *J. Chem. Research*, 1977, (*S*) 324; (*M*) 3636.
[5] J. Polonsky, Z. Varon, and T. Sevenet, *Experientia*, 1975, **31**, 1113.
[6] (a) J. Polonsky, *Proc. Chem. Soc.*, 1964, 292; (b) W. A. C. Brown and G. A. Sim, *ibid.*, p. 293.
[7] H. Hikino, T. Ohta, and T. Takemoto, *Phytochemistry*, 1975, **14**, 2473.
[8] G. Germain, P. Main, and M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.