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# QUASSINOIDS.[1] ISOLATION FROM *SOULAMEA MUELLERI* AND STRUCTURES OF 1,12-DI-O-ACETYL SOULAMEANONE AND $\Delta^2$-PICRASIN B. X-RAY ANALYSIS OF SOULAMEANONE

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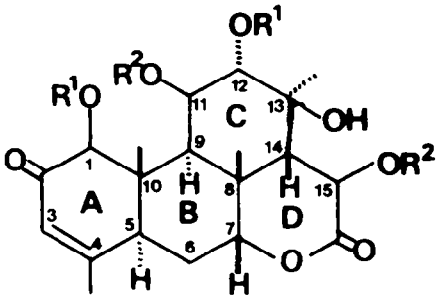
**Abstract** The structures of soulameanone, 1,12-di-O-acetyl soulameanone and $\Delta^2$-Picrasin B, new quassinoids from *Soulamea muelleri* (Simaroubaceae), were determined by spectrometric methods and chemical correlation, and that of Soulameanone confirmed by single crystal X-ray analysis.

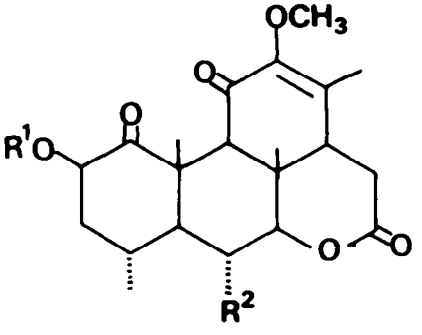
As a continuation of our work on quassinoids,[2] the bitter principles of the plant family Simaroubaceae, we examined the New Caledonian species *Soulamea muelleri* Brongn. et Gris. We report here the isolation, structural elucidation and preliminary antileukaemic evaluation of the following new quassinoids: soulameanone **1** and $\Delta^2$-picrasin B **3** (from the leaf extract), and 1,12-di-O-acetyl soulameanone **2** (from the stem extract). The previously known quassinoids picrasin B **4**[3,4] and 6-hydroxypicrasin B **5**[4,5,6] were also isolated from *Soulamea muelleri*. The structure of soulameanone **1** was determined by spectral means and by single crystal X-ray analysis, the structures of the quassinoids **2** and **3** were established by chemical correlations and spectral analyses.

The dried ground leaves of *Soulamea muelleri* were first defatted with hexane and then extracted several times with hot water. The concentrated aqueous extract was continuously extracted with chloroform. Column chromatography of the evaporated extract on silica gel, and elution with methylene chloride containing increasing amounts of methanol, afforded successively $\Delta^2$-picrasin B **3**, the quassinoids **4** and **5** and soulameanone **1**. Chromatography of a stem extract of *Soulamea muelleri*, prepared by the procedure described for the leaf extract, led to the isolation of the known quassinoids **4** and **5** and of 1,12-di-O-acetyl soulameanone **2**.

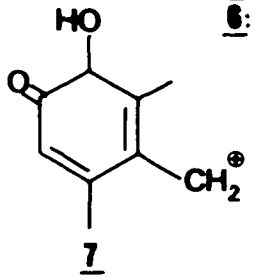
$\Delta^2$-Picrasin B **3** has the composition $C_{21}H_{26}O_6$ ($M^+$ 374). It shows IR bands at 1736 and 1667 $cm^{-1}$.



**1**: $R^1 = R^2 = H$
**2**: $R^1 = Ac$ ; $R^2 = H$
**8**: $R^1 = R^2 = Ac$



**3**: $R^1 = R^2 = H$ ; 2,3 dehydro
**4**: $R^1 = R^2 = H$
**5**: $R^1 = H$ ; $R^2 = OH$
**6**: $R^1 = CH_3$ ; $R^2 = H$ ; 2,3 dehydro



**7**

UV absorption at 256 nm and gives a brown red colour with 2% aqueous ferric chloride. The $^1$H NMR spectrum of **3** was very similar to that of quassin **6** and showed the presence of four methyl groups–two angular, one secondary and one vinyl and one methoxyl. These data indicate that **3** differs from quassin **6** by the presence of a free diosphenol grouping. This small structural modification was substantiated by conversion of **3** to quassin **6** on methylation with diazomethane. Structure **3** was further established by chemical correlation with picrasin B **4**;[3,4] oxidation of the latter with bismuth trioxide gave a diosphenol identical in every respect with the quassinoid **3**. $\Delta^2$-Picrasin B had already been prepared from picrasin B[3] but was not reported as a naturally occurring quassinoid.

Soulameanone **1**. The high resolution mass spectrum led to the molecular formula $C_{20}H_{28}O_8$ and showed significant fragmentation ions corresponding to $C_{20}H_{26}O_7$ ($M^+ - H_2O$), $C_{19}H_{23}O_7$ ($M^+ - H_2O - CH_3$) and $C_{20}H_{24}O_6$ ($M^+ - 2H_2O$). The IR spectrum revealed hydroxyl absorption and two carbonyl bands at 1735 ($\delta$-lactone) and 1645 cm$^{-1}$ ($\alpha,\beta$-unsaturated ketone). In agreement with the formulation of ring A as in **1**, the UV spectrum showed a maximum at 239 nm, the 250 MHz $^1$H NMR spectrum (Table 1) displayed the characteristic signals due to the vinyl methyl, 1-H and 3-H, and the mass spectrum showed the diagnostic peak corresponding to $C_9H_{11}O_3$.[7] The $^1$H NMR spectrum also revealed singlets due to three additional methyl groups and displayed one-proton signals assignable to four additional oxygen-bearing methine groups. Double resonance experiments identified the protons H-7, H-11 and H-12. For example, irradiation of H-11 (m at $\delta$ 4.61) collapsed the H-12 and H-9 doublets to singlets. The triplet-like signal which was assigned to H-7 suggested the absence of a hydroxy-group at C-6. Therefore the remaining signal, the singlet at $\delta$ 4.96, due to an oxygen-bearing carbon was attributed to H-15. The quite unusual absence of spin coupling with H-14 can be explained by the boat conformation of the lactone ring (see below).

The presence of four secondary hydroxyl groups was further substantiated by acetylation experiments. The axial 11-hydroxy groups of this type of quassinoids are known to be difficult to acetylate[8,9] and this accounts for the formation of a mixture of tri- and tetraacetyl derivatives upon treatment of soulameanone **1** with acetic anhydride in pyridine (room temperature, 17 h). Soulameanone is readily acetylated in the presence of 4-(*N*,*N*-dimethylamino)pyridine[10] to give the tetraacetate **8**, $C_{28}H_{36}O_{12}$ ($M^+$ at *m/e* 564). The 250 MHz $^1$H NMR (Table 1) revealed significant downfield shifts for H-1, H-11, H-12 and H-15, which were identified by decoupling experiments. The tetraacetate **8** whose IR spectrum displayed an OH absorption was recovered unchanged after oxidation with Jones' reagent. This, in conjunction with consideration of the number of the oxygen atoms in **1**, indicated that the latter possesses a tertiary hydroxyl group. The location of this group at C-13 was suggested by the absence of a secondary methyl group and the presence of a downfield methyl signal ($\delta$ 1.61) in the $^1$H NMR spectrum of soulameanone.

Unequivocal proof for the structure and relative stereochemistry of soulameanone **1** was provided by single-crystal X-ray analysis. The absolute configura-

Table 1. Proton magnetic resonance spectra at 250 MHz of soulameanone 1 and 1,12-Di-O-acetyl Soulameanone 2 in deuteriochloroform solution containing approximately 20% pyridine-$d_5$ and of 1,11,12,15-Tetra-O-acetyl soulameanone 8 in deuteriochloroform ($\delta$ in ppm, J in Hz)

| Proton position | 1 | 2 | 8 |
|---|---|---|---|
| H-1 | 4.07 s | 5.32 s | 5.33 s |
| H-3 | 6.04 br.s | 6.02 br.s | 6.04 br.s |
| H-5 | 3.05 br.d J = 13 | 3.25 br.d J = 13 | 3.22 br.d J = 12.5 |
| H-7 | 5.28 br.s | 4.87 m | 4.69 m |
| H-9 | 2.28 d J = 5.7 | * | * |
| H-11 | 4.61 m | 4.38 m | 5.31 m** |
| H-12 | 4.13 d J = 6.8 | 4.96 d J = 5 | 5.01 d J = 4 |
| H-15 | 4.96 s | 4.56 d J = 2 | 5.37 d J = 6.4 |
| 4-Me | 1.86 s | 1.94 s | 1.97 s |
| Me | 1.61 s | 1.73 s | 1.72 s |
| | 1.40 s | 1.41 s | 1.25 s |
| | 1.26 s | 1.33 s | 1.21 s |
| OAc | | 2.00 | 2.19 |
| | | 2.00 | 2.15 |
| | | | 2.11 |
| | | | 2.08 |

* obscured ; ** superimposed with H-1.

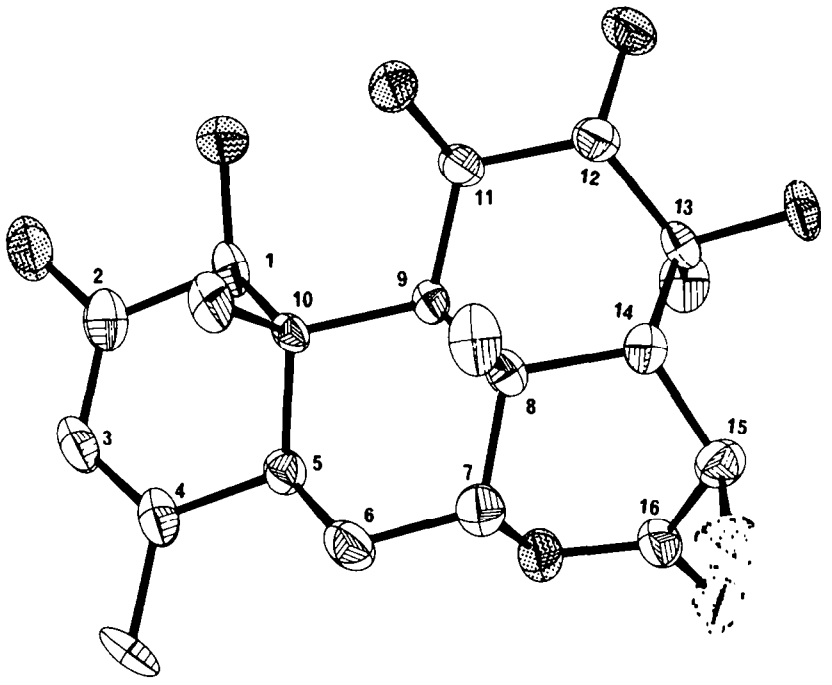



Fig. 1. Molecular structure of soulameanone **1** (dotted ellipsoids denote oxygen atoms).

tion, also represented by **1**, follows from the experimentally proven triterpenoid biogenetic origin of quassinoids.[2]

A view of the molecular conformation is shown in Fig. 1 with ellipsoids drawn at the 50% probability level for the electronic density. The ring junctions are the same as in all quassinoids (A/B *trans*, B/C *trans*, B/D *cis* and C/D *cis*) and the configurations of the hydroxyl substituents are: 1$\beta$-OH, 11$\beta$-OH, 12$\alpha$-OH, 13$\beta$-OH and 15$\beta$-OH. The five OH functions are implicated in an hydrogen bond network. The strongest *intra*-molecular hydrogen bonding is found between the hydroxy groups at C-1 and C-11 [O(1)...O(11) = 2.71 Å] which may contribute to the difficulty in acetylating the 11-OH group on acetylating the other secondary hydroxyls. The 12-OH is *intra*-molecularly hydrogen bonded with 11-OH and 13-OH [O(12)...O(11) = 3.0 Å and O(12)...O(13) = 2.86 Å]. Repulsive interaction is observed between 13-OH and 15-OH [O(13)...O(15) = 4.78 Å]. The 15-OH is *inter*-molecularly hydrogen bonded with the carbonyl group of the $\delta$-lactone (d = 3.12 Å) of an adjacent molecule. This hydrogen bonded geometry induces particular conformational shapes for the rings. Ring A adopts a half-chair conformation, ring B is in the chair form with atoms C(5), C(6), C(9) and C(8) in the mean plane within $\pm$0.02 Å, ring C adopts a boat conformation with C(8), C(14), C(11) and C(12) in the mean plane within $\pm$0.11 Å and C(9) and C(13) lying 0.5 and 0.6 Å respectively above the plane; the $\delta$-lactone ring assumes a very well defined boat conformation with atoms C(8), C(14), C(16) and O [on C(7)] planar within $\pm$0.06 Å and C(7) and C(15) lying 0.64 and 0.54 Å respectively above the plane.

The dihedral angles between H-9 and H-11, and between H-11 and H-12 are 39° and 151° respectively: these values are in agreement with the pattern and coupling constants observed for these protons in the $^1$H NMR spectrum of soulameanone (Table 1). The unusual signal due to H-15 (sharp singlet) can be explained by the boat conformation of the $\delta$-lactone ring and the value (86°) of the dihedral angle between H-14 and H-15 corresponding to a very small coupling constant. In contrast, the H-15 signal in the $^1$H NMR spectrum of 15-hydroxy klaineanone,[9] which differs from soulameanone by the absence of the 13-OH, appears as a doublet (J = 9 Hz). Thus, the observed repulsive interaction between the hydroxyls at C-13 and C-15 of soulameanone seems to be the main cause for the $\delta$-ring to adopting the boat conformation in the crystal and also in solution. The D ring in the tetraacetate **8** probably adopts a different conformation since H-15 appears in its $^1$H NMR spectrum as a doublet (J = 6.4 Hz).

High resolution mass spectrometry established the molecular composition $C_{24}H_{32}O_{10}$ for 1,12-di-O-acetyl soulameanone **2** and showed significant fragmentation ions corresponding to $C_{24}H_{30}O_9$ ($M^+$ $H_2O$), $C_{21}H_{25}O_8$ ($M^+$-$H_2O$-$CH_3$-$C_2H_2O$), $C_{19}H_{23}O_7$ ($M^+$-$H_2O$-$CH_3$-$2C_2H_2O$), $C_{20}H_{26}O_7$ ($M^+$-$H_2O$-$2C_2H_2O$) and to $C_9H_{11}O_2$ (ion 7). Interpretation of these data and the 250 $^1$H NMR spectrum (Table 1) suggested compound **2** to be a diacetate derivative of soulameanone **1**. This was further substantiated by inspection of the $^{13}$C NMR spectrum (Table 2) which displayed four carbonyl carbon signals due to the lactonic, enonic and acetate carbonyls, five oxygen-bearing methine carbons (C-1, C-7, C-11, C-12 and C-15) and one non protonated oxygen-bearing carbon (C-13). The assignments of carbons (by off-resonance proton decoupling technique) were comparable with those of other similar quassinoids.[12] The structure **2** for diacetylsoulameanone was further confirmed by acetylation with acetic

Table 2. $^{13}C$ NMR spectrum of 1,12-Di-O-acetyl soulameanone 2 measured at 22.6 MHz in deuteriochloroform-pyridine $d_5$ (~20%) recorded in ppm downfield from $Me_4Si$

| | | | | | |
|---|---|---|---|---|---|
| C (1) | 85.1 | d | C (12) | 79.8* | d |
| C (2) | 191.5 | s | C (13) | 72.3 | s |
| C (3) | 125.9 | d | C (14) | 61.3 | d |
| C (4) | 162.3 | s | C (15) | 67.1 | d |
| C (5) | 42.9 | d | C (16) | 172.4 | s |
| C (6) | 24.6 | t | $\underline{CH_3}CO$ | 170.5 | s |
| | | | | 170.1 | s |
| C (7) | 71.2 | d | | | |
| C (8) | 38.1 | s | $\underline{CH_3}CO$ | 20.7 | q |
| | | | | 20.7 | q |
| C (9) | 42.9 | d | 4-Me | 22.2 | q |
| C (10) | 46.2 | s | 8-Me | 27.2 | q |
| | | | 10-Me | 13.0 | q |
| C (11) | 78.5* | d | 13-Me | 22.2 | |

*These signals may be interchanged.

anhydride in presence of 4-(*N*,*N*-dimethylamino-) pyridine.[10] The resulting tetraacetate was identical with the tetra-acetate **8** obtained from soulameanone by TLC, mass spectra and 250 MHz $^1H$ NMR. The assignment of the protons of **2** (Table 1) was achieved by extensive decoupling experiments. Thus, irradiation of H-11 (m at $\delta$ 4.38) collapsed the H-12 doublet to a singlet and irradiation at $\delta$ 2.40 (H-14) converted the doublet at $\delta$ 4.56 (H-15) to a singlet. Comparison of the $^1H$ NMR spectra of soulameanone **1** and diacetyl soulameanone **2** showed that H-1 and H-12 were significantly deshielded in **2**, thus allowing the assignment of the acetoxy groups to positions 1 and 12.

Soulameanone **1** did not show significant inhibitory *in vivo* activity against the P-388 lymphocytic leukemia in the mouse.[13] This confirms previous findings[14] that a part of the $\Delta^3$-oxo moiety in ring A, an ester group at C-15 (or and C-6) and an epoxymethano bridge between C-8 and C-11 or between C-8 and C-13 are structural requirements for *in vivo* antileukaemic activity in the P-388 system.

## EXPERIMENTAL

Melting points were determined using a Kofler hot-stage microscope and are uncorrected. Optical rotations were determined at room temperature on a Roussel–Jouan Quick polarimeter. IR spectra were recorded with a Perkin Elmer model 257 spectrometer. The UV spectra were measured with a Spectronic model 505 spectrometer (Bausch and Lomb). Electron impact mass spectra were taken on a MS 50-AEI spectrometer The 250 MHz $^1H$ NMR spectra were recorded on a Cameca spectrometer. The $^{13}C$ NMR spectrum was measured with a Bruker HXE 90 (22.63 MHz) spectrometer.

*Extraction and isolation of $\Delta^2$-picrasin B*3, *picrasin B*4, *6-hydroxy-picrasin B* **5** *and soulameanone* **1**

The plant material was collected in 1979 in New Caledonia and represented the leaves of *Soulamea muelleri* Brongn. The air-dried, ground leaves (766 g) were defatted by percolation with hexane at room temperature. The mass was then stirred for several hours with hot water (70–75°), separated by filtration *in vacuo* and resuspended in fresh hot water. This was repeated several times until the filtrate was no longer bitter. The combined aqueous extracts were concentrated *in vacuo* and then continuously extracted with chloroform. Evaporation of the solvent yielded a brown foam (10.6 g) which was chromatographed on silica gel (60 Merck) (500 g) using dichloromethane containing increasing amounts of methanol as eluent. Fractions of 200 ml each were collected and combined on the basis of TLC (silica gel F-254) similarity. Fractions eluted with $CH_2Cl_2$ containing 2% MeOH gave, upon evaporation of solvent, 321 mg of a crystalline residue which was recrystallized from ethyl acetate to give $\Delta^2$-picrasin B **3**. Fractions eluted with $CH_2Cl_2$ containing 3% of methanol gave picrasin B **4** and 6-hydroxypicrasin B **5** which were separated and purified by preparative TLC over silica gel 60 PF 254 (Merck) using 96:4 ethyl acetate-methanol and detecting by UV. Their identification with authentic samples was established by m.p., TLC, and MS comparison. Fractions eluted with $CH_2Cl_2$ containing 8% of MeOH yielded crude soulameanone **1** (1.2 g) which was purified by preparative TLC (9:1, EtOAc MeOH).

*$\Delta^2$-Picrasin B* **3** Colourless needles from MeOH, m.p. 248–250°; $[\alpha]_D^{22}$ + 31.1° (c 0.90; MeOH $CHCl_3$, 2:1). IR (Nujol): 1736 and 1667 $cm^{-1}$. UV (EtOH). $\lambda_{max}$ 256 nm ($\varepsilon$ 10,000). 60 MHz $^1H$ NMR ($CDCl_3$:pyridine-$d_5$): $\delta$ 1.04 (d, 3H, J = 7 Hz, 4-$CH_3$); 1.20 (s, 3H, 8-$CH_3$); 1.63 (s, 3H, 10-$CH_3$) 1.86 (s, 3H, 13-$CH_3$); 3.03 (s, 1H, 9-H); 3.77 (s, 3H, $OCH_3$); 4.37 (m, 1H, 7-H); 5.72 (d, J = 2 Hz, 3-H). MS: $M^+$ 374. Calc. *Anal.* Found: C, 66.96; H, 6.93% for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. $\Delta^2$-Picrasin B **3** (39 mg) in MeOH (4 ml) was methylated with an excess of $CH_2N_2$ in ether. After evaporation of solvent and purification on preparative TLC, pure quassin **6** was obtained.

Picrasin **4** (138 mg) in EtOAc (8 ml) was oxidised by $Bi_2O_3$ (250 mg) as described in Ref. 3. After the usual work-up, the product was purified by preparative TLC to give $\Delta^2$-picrasin B (89 mg) identical in every respect with the natural quassinoid **3**.

Soulameanone **1**. Colourless prisms from MeOH-acetone; m.p. 263–265°, $[\alpha]_D^{22}$ + 101° (c 1.01, MeOH $CHCl_3$ 2:1). IR (Nujol). 3300, 1730 and 1645 $cm^{-1}$. UV (EtOH). $\lambda_{max}$ 239 nm ($\varepsilon$ 10,400). Found: C 60.43; H 7.19%. Calc. for $C_{20}H_{28}O_8$: C 60.59; H 7.12. MS: $M^+$ at *m/e* 396.1738 and other major ions were observed at *m/e* (% relative intensity), 378.1614 (51), 363.1417 (31), 360.1582 (3.4) and 151.0751 (16).

*Tetraacetate* **8**. Soulameanone **1** (70 mg) in acetic anhydride (2 ml) and pyridine (2 ml) was set aside at room temp overnight. Working up in the usual manner gave a product (70 mg) which was homogenous on TLC but whose $^1H$ NMR spectrum showed it to be a mixture of a tri- and tetra-acetate. This mixture was then re-acetylated with acetic anhydride (0.5 ml), 4-*N*,*N*-dimethyl-aminopyridin (2 mg)[10] and 0.5 ml $(Et)_3N$ for 1 h. Usual work-up yielded tetraacetate **8** (48 mg). MS. $M^+$ at *m e* 564 and ions at *m e* 522 ($M^+$ − 42).

Table 3. Fractional atomic coordinates and anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms, with estimated standard deviations in parentheses, given in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

| ATOM | x | y | z | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | "B" |
|---|---|---|---|---|---|---|---|---|---|---|
| C ( 1) | 6404 (11) | 4325 ( 7) | 6909 ( 4) | 132 (17) | 39 ( 6) | 8 ( 2) | 13 ( 9) | -2 ( 5) | 4 ( 3) | 2.2 |
| C ( 2) | 6813 (12) | 4116 ( 7) | 6139 ( 4) | 140 (20) | 44 ( 6) | 14 ( 2) | 17 (10) | 5 ( 6) | 6 ( 3) | 2.7 |
| C ( 3) | 6706 (13) | 3682 ( 7) | 5749 ( 4) | 161 (22) | 56 ( 7) | 9 ( 2) | 1 (11) | -1 ( 6) | -3 ( 3) | 2.9 |
| C ( 4) | 6656 (13) | 3492 ( 6) | 6043 ( 4) | 176 (22) | 29 ( 6) | 11 ( 2) | 10 (10) | 5 ( 6) | 0 ( 3) | 2.5 |
| MI ( 4) | 2177 (13) | 2991 ( 8) | 5608 ( 4) | 181 (22) | 66 ( 8) | 14 ( 3) | -11 (12) | -24 ( 6) | -14 ( 4) | 3.5 |
| C ( 5) | 3355 (12) | 3695 ( 6) | 6795 ( 4) | 123 (18) | 28 ( 6) | 12 ( 2) | -7 ( 9) | -2 ( 5) | 1 ( 3) | 2.1 |
| C ( 6) | 1914 (12) | 3843 ( 7) | 6994 ( 4) | 105 (19) | 60 ( 7) | 14 ( 2) | -1 (10) | -11 ( 6) | -2 ( 3) | 2.8 |
| C ( 7) | 1137 (14) | 3872 ( 7) | 7766 ( 4) | 91 (19) | 50 ( 7) | 16 ( 2) | 9 (10) | -1 ( 5) | 2 ( 3) | 2.5 |
| C ( 8) | 2256 (14) | 4068 ( 8) | 8173 ( 4) | 84 (17) | 55 ( 8) | 11 ( 2) | 9 ( 8) | -3 ( 5) | -1 ( 3) | 1.9 |
| MI ( 8) | 1505 (15) | 5011 ( 8) | 8073 ( 4) | 159 (21) | 54 ( 6) | 20 ( 2) | 53 (11) | 5 ( 6) | 7 ( 3) | 3.0 |
| C ( 9) | 4217 (14) | 4526 ( 6) | 7910 ( 3) | 109 (17) | 15 ( 5) | 9 ( 2) | 0 ( 8) | -2 ( 5) | 3 ( 3) | 1.6 |
| C (10) | 4491 (10) | 4616 ( 6) | 7101 ( 3) | 91 (16) | 23 ( 5) | 8 ( 2) | 0 ( 8) | -8 ( 5) | 2 ( 3) | 1.6 |
| MI (10) | 4045 (13) | 5702 ( 8) | 6757 ( 4) | 213 (23) | 17 ( 5) | 13 ( 2) | 11 (10) | -7 ( 6) | 8 ( 3) | 2.7 |
| C (11) | 5607 (12) | 5135 ( 6) | 6346 ( 4) | 119 (19) | 32 ( 6) | 12 ( 2) | -8 ( 9) | -8 ( 5) | 0 ( 3) | 2.2 |
| C (12) | 5126 (11) | 5175 ( 6) | 9120 ( 4) | 108 (17) | 36 ( 6) | 14 ( 2) | -9 (10) | -8 ( 6) | 1 ( 3) | 2.3 |
| C (13) | 3946 (11) | 4267 ( 6) | 9246 ( 4) | 102 (16) | 35 ( 6) | 9 ( 2) | 9 ( 9) | -1 ( 5) | -3 ( 3) | 2.0 |
| MI (13) | 4833 (12) | 3141 ( 6) | 9310 ( 4) | 137 (20) | 27 ( 6) | 18 ( 2) | 29 ( 9) | 7 ( 6) | 2 ( 3) | 2.5 |
| C (14) | 2174 (11) | 4400 ( 6) | 8968 ( 4) | 96 (17) | 29 ( 5) | 13 ( 2) | 12 ( 9) | 5 ( 5) | 0 ( 3) | 2.0 |
| C (15) | 899 (12) | 3493 ( 7) | 9141 ( 4) | 103 (19) | 41 ( 6) | 18 ( 3) | -7 (10) | 7 ( 6) | -3 ( 3) | 2.6 |
| C (16) | 1162 (12) | 2573 ( 7) | 8660 ( 4) | 102 (19) | 56 ( 7) | 12 ( 2) | -9 (10) | 4 ( 6) | -5 ( 3) | 2.6 |
| O ( 17) | 7644 ( 8) | 5147 ( 5) | 7124 ( 3) | 110 (12) | 63 ( 5) | 18 ( 2) | -21 ( 7) | -1 ( 4) | -2 ( 2) | 3.0 |
| O ( 18) | 8061 ( 8) | 4341 ( 5) | 9889 ( 3) | 146 (14) | 97 ( 6) | 13 ( 2) | -6 ( 9) | 1 ( 4) | 4 ( 3) | 3.8 |
| O ( 19) | 1474 ( 8) | 2765 ( 4) | 7956 ( 3) | 165 (14) | 43 ( 4) | 14 ( 2) | -17 ( 7) | 6 ( 4) | -2 ( 2) | 2.8 |
| O ( 20) | 1115 (10) | 1616 ( 5) | 8862 ( 3) | 271 (20) | 51 ( 5) | 23 ( 2) | -21 ( 9) | 27 ( 5) | 0 ( 3) | 4.3 |
| O ( 21) | -907 ( 8) | 3456 ( 5) | 9631 ( 3) | 71 (11) | 66 ( 6) | 30 ( 2) | -1 ( 8) | 1 ( 4) | -9 ( 3) | 3.9 |
| O ( 22) | 3034 ( 8) | 4431 ( 4) | 10067 ( 3) | 166 (14) | 51 ( 5) | 8 ( 1) | 6 ( 7) | 7 ( 4) | -2 ( 2) | 2.7 |
| O ( 23) | 6743 ( 8) | 5207 ( 5) | 9509 ( 3) | 101 (12) | 74 ( 5) | 17 ( 2) | -17 ( 7) | -8 ( 4) | -7 ( 2) | 3.1 |
| O ( 24) | 5950 ( 9) | 6210 ( 4) | 8139 ( 3) | 223 (16) | 25 ( 4) | 16 ( 2) | -33 ( 7) | 2 ( 4) | 1 ( 2) | 3.1 |

504 ($M^+$ 60), 462 ($M^+$-60-42), 420 ($M^+$-60-42-42), 405 ($M^+$ 60 42 42 15).

*Crystal data and crystallographic measurements*

A thin plate of soulameanone **1**, approximate size 0.5 × 0.2 × 0.02 mm, was mounted on a four-circle automatic diffractometer operating with CuK$\alpha$ radiation ($\lambda$ = 1.5418 Å). The system is orthorhombic, space group $P2_12_12_1$ (Z = 4) with cell parameters: a = 7.620; b = 12.532 and c = 19.273 Å. A total of 1339 reflections were recorded above the 2 $\sigma$ background level at a speed of 0.02°. $s^{-1}$ over a 1.2° scanning range by the $\theta$ 2 $\theta$ scan technique, to a $2\theta$ maximum of 120°. The structure was solved by the use of the multisolution technique[11] and the refinement conducted with isotropic, then anisotropic, thermal factors for the heavy atoms by the least-squares block diagonal procedure to a final R value of 6.7%. All hydrogen atoms, except those of one methyl carbon, were located on successive Fourier difference syntheses. Final atomic coordinates for the non-hydrogen atoms together with their estimated standard deviations (e.s.d.) are given in Table 3. Tables of calculated and observed structure amplitudes and anisotropic thermal parameters for the non-hydrogen atoms are available on request from the authors.

*Extraction and isolation of* 1,12-*di*-O-*acetyl soulameanone* **2**

The plant material was collected in 1974 in Tiébaghi (New Caledonia) and represented the stems of *Soulamea muelleri* Brogn. The powdered stem (400 g) was extracted as described above for the leaves to yield a chloroform soluble residue (2.7 g) which was chromatographed on silica gel (270 g) Fractions eluted with chloroform containing 2% of methanol afforded picrasin B **4** (520 mg), fractions eluted with chloroform containing 3% of methanol gave 6-hydroxy-picrasin B **5** (270 mg) and those eluted with chloroform containing 5% of methanol gave crude 1,12-di-O-acetyl soulameanone **2** (180 mg) which was purified by crystallisation.

1,12-Di-O-*acetyl soulameanone* **2**. Colourless needles from ethyl acetate, m.p. 265–268°. UV (EtOH): $\lambda_{max}$ 241 nm ($\varepsilon$ 10,100) MS: $M^+$ at *m/e* 480.000 and other major ions were observed at *m/e* (% relative intensity) 462.1870 (1.1), 405.1555 (7.2), 378.1671 (16.5), 363.1451 (61.5), 151.0757 (6.9) and 135.0814 (16.1). Acetylation of 2 (18 mg) with $Ac_2O$ (0.03 ml), $Et_3N$ (0.03 ml) and 4-(*N,N*-dimethylamino)pyridin (1 mg) afforded the tetra-acetate **8**.

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