

elution with EtOAc–C₆H₆ (2.5:7.5) afforded 2- α -hydroxyursolic acid, mp 243–44° *R_f*, 0.60 (MeOH–CHCl₃) (1:9), diacetate mp 197°, methyl ester mp 207–208°, [α]_D + 48 (1.1, CHCl₃), methyl ester acetate mp 143–145°. MS of the methyl ester showed M⁺ 486, 262 (DE ring fragment through RDA fission), 223 (AB ring fragment RDA), 203 (262–COOMe). NMR of methyl ester diacetate in CCl₄ showed δ 1.94 and 2.02 (OCOMe), 3.60 (COOMe) and a doublet at 4.68 (*J* 10 Hz) (C₃-H) indicating trans diaxial protons at C₂ and C₃. Confirmed by direct comparison (TLC, IR, NMR and MS). This is the second report of the occurrence of 2- α -hydroxyursolic acid in Myrtaceae; the first [5] described its co-occurrence with maslinic acid in *Psidium guajava* leaves. The presence

of compounds belonging to three related skeletons together in *Callistemon* is noteworthy.

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3-ETHYL-7-HYDROXYPHthalIDE FROM *FORSYTHIA JAPONICA*

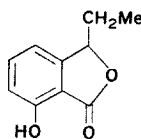
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Key Word Index—*Forsythia japonica*; Oleaceae; essential oil; 3-ethyl-7-hydroxyphthalide.

Plant. *Forsythia japonica* Makino, stem bark.
Source. Collected from the outskirts of Osaka-Fu, Japan.
Uses. Medicinal.
Previous work. Leaves of *F. coreana* Nakai and *F. suspensa* Vahl [1]. Bark and leaves of several *Forsythia* species [2].
Present work. In continuation of our investigations on the essential oil of *F. japonica*, we now report the occurrence of 3-ethyl-7-hydroxyphthalide (1).



(1)

The essential oil of the stem bark of *F. japonica* deposited a crystalline constituent, C₁₀H₁₀O₃, mp 78°, [α]_D²⁵ + 1.87 (1.01% in EtOH). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 235, 300 nm (log ϵ 2.34, 1.90) almost superimposable with that of synthetic 3-ethyl-7-hydroxyphthalide [3]. NMR: $\delta_{\text{ppm}}^{\text{CCl}_4}$ (60 MHz, i.s. TMS) 1.03 (3H, *t*, –CH₂–Me), 1.89 (2H, *m*, –CH₂–Me), 5.35 (1H, *t*, –CH–O–CO–), 6.82 (2H, *d*, aromatic

H), 7.44 (1H, *t*, aromatic H), 7.79 (1H, broad *s*, –OH). IR: $\nu_{\text{max}}^{\text{KBr}}$ 3500, 3020, 1740, 1605, 1478, 1195 cm^{–1}. MS: *m/e* (abundance %) 178 (37.8), 149 (100.0), 121 (33.5), 93 (11.7), 65 (16.5).

The acetate (C₆H₅N–Ac₂O) was purified by Al₂O₃ column chromatography. NMR: $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.99 (3H, *t*, –CH₂–Me), 1.88 (2H, *m*, –CH₂–Me), 2.34 (3H, *s*, –O–CO–Me), 5.24 (1H, *t*, –CH–O–CO–), 7.08 (2H, *t*, aromatic H), 7.55 (1H, *t*, aromatic H). IR: $\nu_{\text{max}}^{\text{NaCl}}$ 1768, 1370, 1189 cm^{–1}. Methylation with CH₃N₂ gave the ether. NMR: $\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.99 (3H, *t*, –CH₂–Me), 1.88 (2H, *m*, –CH₂–Me), 3.95 (3H, *s*, ϕ –O–Me), 5.22 (1H, *t*, –CH–O–CO–), 6.86 (2H, *d*, aromatic H), 7.52 (1H, *t*, aromatic H). IR: $\nu_{\text{max}}^{\text{NaCl}}$ 1288, 1040 cm^{–1}. MS: *m/e* 192 (19.5), 175 (5.0), 162 (19.5), 163 (100.0), 146 (29.0), 135 (24.3), 105 (11.5), 77 (20.5). The compound was thus shown to be 3-ethyl-7-hydroxyphthalide (1).

This is its first isolation from a plant source and is significant from the biogenetic point of view since all phthalides, so far isolated from plants, have the same skeleton or a modification thereof.

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ENT-16-KAUREN-19-OL FROM COFFEE

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Key Word Index—*Coffea arabica*; Rubiaceae; CMR spectrum; diterpenoid; *ent*-16-kauren-19-ol.

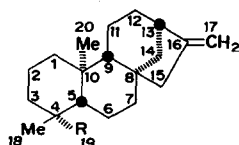
On examination of the sterols of coffee beans (*Coffea arabica* L.) a small amount of a diterpene alcohol in the form of its acetate was encountered [1]. Its structure was tentatively suggested as being 15-abieten-13 β ,19-diyl diacetate. However, its CMR spectrum was not in harmony with the proposed structure. Thus, the compound proved to contain 22 carbon atoms, two of which constituted an acetoxy group (singlet at 171.4 ppm and quartet at 21.0 ppm) attached to a methylene group (triplet at 67.2 ppm). Furthermore, the presence in the CMR spectrum of resonances due to two additional methyl groups (quartets at 27.6 and 18.1 ppm), an exocyclic methylene group (singlet at 155.8 ppm, triplet at 103.0 ppm) and three tetrasubstituted non-oxygenated carbon atoms (singlets at 44.2, 39.2 and 37.1 ppm) implied that the unknown diterpene acetate was 16-kauren-19-yl acetate. This was confirmed by direct comparison with an authentic sample (mmp, $[\alpha]_D$, IR, PMR, CMR and MS).

Ent-16-kauren-19-ol has not been detected in coffee before. From a biogenetic point of view its presence is of interest, since the major diterpenoids of coffee, cafestol [2,3] and kahweol [4], are of the kaurene type. It is also interesting to note that *ent*-16-kauren-19-ol, previously isolated from a few natural sources, e.g. barley [5] and *Abrotanella nivigena* [6], is an intermediate in the biosynthesis of the gibberellins [7,8] and shows a gibberellin-like biological activity [9].

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- (1) R = CH₂OAc
- (2) R = CH₂OH