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THE CONSTITUENTS OF *CACALIA DECOMPOSITA* A. GRAY—IV

STRUCTURE OF DECOMPOSTIN[1]

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Abstract—Decompostin, a constituent of *Cacalia decomposita* A. Gray has been shown to be a sesquiterpene of the eremophylane series with structure Ia.

IN PREVIOUS papers,[2–4] the isolation and the structure proofs of several constituents of *Cacalia decomposita* A. Gray were described. We now wish to report the isolation and chemical study of decompostin isolated from the same source.

Decompostin (Ia; $C_{17}H_{20}O_5$) m.p. 183–184°, was isolated from the hexane extract of the plant. Its UV spectrum (λ_{max} 254, 302 mμ; ε, 4600, 16,200) indicates the presence of a highly conjugated system. Decompostin (Ia) has IR bands at 1740, 1670, 1620, 1600 and 1540 cm^{-1}. It forms a dark red 2,4-dinitrophenylhydrazone which does not show the IR band of Ia at 1670 cm^{-1}. This fact, together with its UV absorption (λ_{max} in $CHCl_3$; 410 mμ; ε, 31,600), indicates the presence of an α,β-unsaturated ketone.

Like other constituents of *C. decomposita*[2–4] decompostin (Ia) possesses a furane ring with a Me group substituted in a β position as indicated by its spectral properties. The NMR spectrum* of Ia exhibits a Me signal on a furane ring at 1·95 (doublet, J = 1·1 c/s) and a furane ring proton at 7·43 (quartet, J = 1·1 c/s).[5]

The NMR spectrum of decompostin (Ia) exhibits, besides the signals assigned to a Me and an hydrogen in a furane ring, three Me signals. A secondary Me group is responsible for a doublet at 0·97 (J = 7 c/s). Two singlets at 1·08 and 2·20 were ascribed to an angular Me group and an Ac group, respectively. The chemical shift of a singlet at 6·32 (1H) attributed to the proton on the carbon carrying the Ac group, suggests that the latter is in an allylic position to a double bond. A triplet centered at 7·00 (1H, J = 4 c/s) is assigned to a vinylic hydrogen on a trisubstituted double bond and in α-position to a methylene group.

Catalytic hydrogenation of Ia over Pd–C gives dihydrodecompostin (IIa). Its UV absorption (λ_{max} 278 mμ; ε, 14,400) and the presence of a strong carbonyl band at 1677 cm^{-1} in its IR spectrum indicates that IIa contains a dienone grouping.[6] Other IR bands at 1740 and at 1610 cm^{-1} correspond to an Ac group and C═C double bonds, respectively.

Dihydrodecompostin (IIa) affords a red 2,4-dinitrophenylhydrazone. The slight hypsochromic shift observed in the UV absorption of the latter (λ_{max} in $CHCl_3$; 392 mμ; ε, 33,100) compared with that shown by the 2,4-dinitrophenylhydrazone of

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* The NMR spectra were determined by Mr. Eduardo Díaz on a Varian A-60 spectrometer in $CDCl_3$ solution, using tetramethylsilane as internal reference. All chemical shifts are reported in ppm as δ values (c/s 60).

Ia, and the shift of the IR band from 1670 cm^{-1} in Ia to 1677 cm^{-1} in the IR spectrum of IIa indicates that the ketone in Ia is cross conjugated. The trisubstituted double bond of decompostin (Ia) is saturated in its dihydroderivative (IIa) since the triplet found at 7·00 in the NMR spectrum of Ia is absent in that of IIa. The NMR spectrum of dihydrodecompostin (IIa) shows the characteristic signals of a proton and a Me group substituted in the furane ring (quadruplet, 1H at 7·37; doublet, 3H at 1·94). When dihydrodecompostin (IIa) is hydrogenated with Adams catalyst, tetrahydrodecompostin (III) is formed. Its UV spectrum (λ_{max} 278 mμ; ε, 260) and an IR band at 1720 cm^{-1} indicate the presence of a saturated 6-membered ketone. In the above hydrogenation the furane ring is partially saturated and probably the double bond which was conjugated with the keto group. The NMR spectrum of III confirms this assumption. It still shows the signal of a Me group substituted in a furane ring at 1·83 (doublet, $J = 1·1$ c/s) and that of a α-furane proton at 7·12 (quadruplet, $J = 1·1$ c/s). The displacement of the singlet corresponding to the proton on the carbon bearing the Ac group to higher field (5·92) demonstrates that the allylic bond is saturated. A new proton signal appears at 4·46 (broad singlet) corresponding to the hydrogen at C-8.

Saponification of dihydrodecompostin (IIa) affords the alcohol IIb. It has IR bands at 3650 cm^{-1} (OH group) and a CO band at 1665 cm^{-1} (α,β-unsaturated 6-membered ketone). The singlet at 2·20 in the NMR spectrum of dihydrodecompostin (IIa) ascribed to the Ac group is absent in the NMR spectrum of IIb. Furthermore, the signal at 6·37 in IIa, assigned to a proton on the carbon carrying the Ac group is not present in the NMR spectrum of IIb, instead a new signal appears at 4·97 (broad singlet) attributed to the proton on the carbon bearing the OH group.

Acetylation of IIb with acetic anhydride–pyridine affords a new acetate which must be epimeric at C-10 with dihydrodecompostin (IIa). It shows IR bands at 1724 cm^{-1} (Ac group) and at 1670 cm^{-1} (α,β-unsaturated 6-membered ketone). The OH group of desacetyldihydrodecompostin (IIb) was oxidized with chromium trioxide in pyridine yielding the enedione (IVa). The crude product had IR bands at 1675, 1615 and 1520 cm^{-1}. It affords a mono-2,4-dinitrophenylhydrazone (IVb; λ_{max} in $CHCl_3$; 396 mμ; ε, 27,500). This derivative shows in the IR spectrum a band at 1675 cm^{-1} of an α,β-unsaturated 6-membered ketone. The keto group responsible for the formation of the 2,4-dinitrophenylhydrazone is the same already present in decompostin (Ia) and its dihydroderivative (IIa) since these products readily give this derivative. These results confirm the relative position of the ketone and the acetate groups in decompostin (Ia) and the assumption that the acetate group is allylic to the furane ring.

LAH reduction of dihydrodecompostin (IIa) affords the diol V. It exhibits the characteristic UV furane absorption[5] (λ_{max} 222 mμ; ε, 7700) and IR bands at 1545 and 1620 cm^{-1}. In the IR spectrum it also shows a band at 3615 cm^{-1} (OH groups) and no absorption in the CO region. The fact that the diol V shows clearly the presence of the furane ring confirms the relative position of the ketone with the furane ring in decompostin (Ia). In the NMR spectrum of V, a broad signal is observed at 4·4 (2H) attributed to the protons attached to the carbon atoms bearing the OH groups.

When decompostin (Ia) is treated with N-bromosuccinimide a bromo derivative (VI) is formed. The triplet present in the NMR spectrum of Ia at 7·00 assigned to the vinylic proton at C-1 has been replaced by a doublet at 7·08 ($J = 6$ c/s) in the NMR spectrum of VI and a new multiplet appears at 4·94 which is ascribed to the hydrogen on the carbon bearing the bromine atom. This clearly indicates that the bromine atom is substituted at C-2 and vicinal to a methylene group. Bromodecompostin (VI) was treated with silver nitrate in aqueous t-butyl alcohol and the crude product obtained after chromatography on basic alumina gave a new compound ($C_{17}H_{18}O_5$; VII). Its UV maxima (λ_{max} 258, 320 mμ; ε, 6600, 9300) and IR bands at 1740 cm^{-1} (Ac group), at 1668 cm^{-1} (α,β-unsaturated 6-membered ketones) and 1600 cm^{-1} (C═C double bonds) indicate that a new ketonic group has been formed at C-2, conjugated with the C-1 (10) double bond. The NMR spectrum of the derivative VII confirms this assumption since the C-1 vinylic hydrogen responsible for the triplet at 7·00 in the NMR spectrum of decompostin (Ia) and for the doublet at 7·08 in the NMR spectrum of bromodecompostin (VI) appears as a singlet at 6·80 in VII. The latter also shows a doublet at 1·1 ($J = 7$ c/s) (secondary Me group) and singlets at 1·30 (3H, angular Me group) at 1·98 (3H, furane Me group), at 2·25 (3H, Ac group), at 6·45 (1H, C-6 hydrogen), at 6·80 (1H, C-1 proton), at 7·62 (broad, 1H, furane proton). The remaining three hydrogens attached to C-3 and C-4 are responsible for a broad signal centered at 2·43.

Treatment of decompostin (Ia) with phosphoric acid in acetic anhydride gives VIII ($C_{19}H_{20}O_4$). The structure of this product was deduced from its spectral features. The UV spectrum (λ_{max}, 216, 253, 260, 329; ε, 16,200, 12,000, 11,700, 26,300) indicates a highly conjugated system. It shows IR bands at 1778 cm^{-1} (phenolic acetate) and at 1668 cm^{-1} (α,β-unsaturated ketone). The NMR spectrum of VIII has a doublet at 1·08 (secondary Me group), but the singlet due to the angular Me group, present in decompostin (Ia) and its derivatives so far described is absent, indicating an aromatization of the central ring of decompostin (Ia). Four singlets appear at 2·43, 2·56, 2·59 and 2·81 which are assigned to an aromatic and a furane Me groups, a phenolic acetate and an Ac group. The fact that the doublet at 1·08 is still present, indicates that VIII is not fully aromatic. The NMR spectrum of VIII also shows a doublet and a multiplet corresponding to two vinylic protons centered at 6·67 and 6·15, respectively. The signal at 7·43 ascribed to the α-furane proton found in the NMR spectrum of decompostin (Ia) is not present in the spectrum of VIII. Therefore, besides the aromatization of the central ring of Ia a characteristic acylation at the α position in the furane ring was produced.[3,6] The mass spectrum* of VIII shows a fragmentation pattern similar to that exhibited by IX, which was obtained by treatment of bisdehydrocacalol acetate (X)[2] with acetic anhydride and phosphoric acid. The derivative VIII shows a small parent peak at 312 *m/e* and a peak due to the loss of two hydrogen atoms at 310 *m/e*. The peaks observed in the mass spectra of VIII and IX are similar, although VIII exhibits peaks two *m/e* higher than those observed in the spectrum of IX up to 197 *m/e*.

The evidence so far described does not distinguish between structures Ia and Ib for decompostin. Structure Ia could be selected on the basis of biogenetic considerations. In this manner it is related to the natural products which belong to the furanoeremophylane system.[5,7–9] This assumption was confirmed by correlation of decompostin (Ia) with furanoeremophylone (XI). Zinc–pyridine reduction[10] of Ia gives a ketone characterized as its 2,4-dinitrophenylhydrazone. The latter is identical

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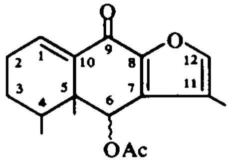
* Mass spectra were determined by Mr. Eduardo Cortés on a Hitachi Perkin-Elmer spectrometer.

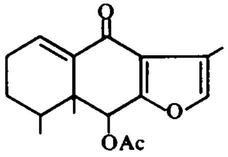
TABLE 1

	Acetate	C-4 Me	C-5 Me	C-11 Me	C-1 H	C-2 H	C-6 H	C-8 H	C-12 H
Decompostin (Ia)	s, 2·20	d, 0·97	s, 1·08	d, 1·95	t, 7·00		s, 6·32		q, 7·43
Dihydrodecompostin (IIa)	s, 2·20	d, 0·93	s, 0·95	d, 1·94			s, 6·37		q, 7·37
Tetrahydrocompostin (III)	s, 2·10	d, 0·82	s, 1·06	d, 1·83			s, 5·92	s, 4·46	q, 7·12
Desacetyldihydrodecompostin (IIb)		d, 0·84	s, 1·10	d, 2·12			s, 4·97		q, 7·40
Epi-dihydrodecompostin (IIc)	s, 2·08	d, 0·86	s, 1·07	d, 2·03			s, 6·27		q, 7·40
Diol (V)		d, 1·10	s, 0·94	d, 2·08					q, 7·12
Bromodecompostin (VI)	s, 2·27	d, 1·08	s, 1·14	d, 2·00	d, 7·08	m, 4·94	s, 6·44		q, 7·52
Ketodecompostin (VII)	s, 2·25	d, 1·10	s, 1·30	s, 1·98	s, 6·80		s, 6·45		s, 7·62

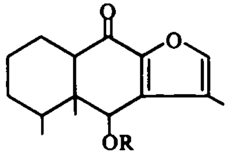
s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.



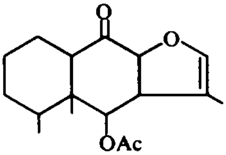
Ia



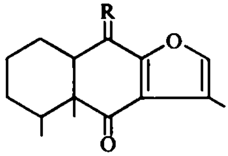
Ib



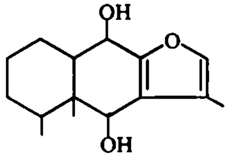
II a, R = Ac
b, R = H
c, R = Ac



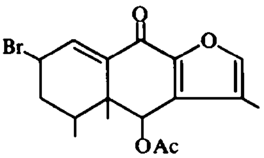
III



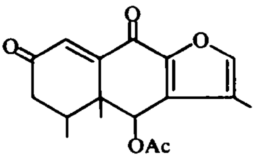
IV a, R = O
b, R = DNPH



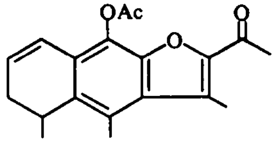
V



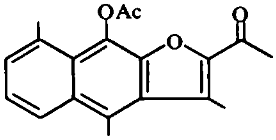
VI



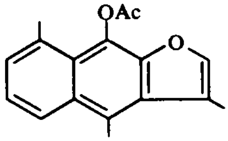
VII



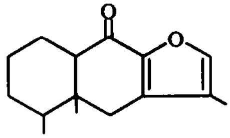
VIII



IX



X



XI

with the 2,4-dinitrophenylhydrazone of furanoeremophylone (XI).* Therefore decompostin possesses structure Ia with its 4 and 5 asymmetric centers as in XI.[7,11] In Table 1, the NMR spectral data of decompostin (Ia) and several of its derivatives described in this paper are summarized.

EXPERIMENTAL

M.ps are uncorrected. The chromatograms were carried out on alumina Alcoa F-20 (Alcoa Chemicals) washed with AcOEt. UV spectra were determined on a Beckman DK2 spectrophotometer in 95% EtOH soln; IR were run in $CHCl_3$ on a Perkin-Elmer double beam spectrophotometer. Rotations were determined in $CHCl_3$ soln at 20°. The microanalyses were performed by Dr. Franz Pascher, Bonn, Germany. We are indebted to Syntex, S.A., for the determination of the rotations.

Isolation of decompostin (Ia). The ground roots of *Cacalia decomposita* (5·7 Kg) were extracted with hexane under reflux for 14 hr. The extract was filtered, evaporated to dryness, treated with pentane and

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* We are grateful to Dr. L. Novotný for a sample of furanoeremophylone.

left overnight. The crystalline product was collected and washed with pentane. yield 18 g, m.p. 177–178°.* Further crystallizations from acetone–hexane furnished pale yellow prisms, m.p. 183–184°; $[\alpha]_D$ +60°; λ_{max}; 254. 302 mμ; ε, 4600, 16,200; IR bands at 1740 cm^{-1} (Ac group), at 1670 cm^{-1} (cross conjugated cyclohexanone), at 1620, 1600 and 1540 cm^{-1} (C=C double bonds). (Found: C, 70·96; H, 6·96; O, 22·42. Calc. for $C_{17}H_{20}O_4$: C, 70·81; H, 6·99; O, 22·20%.)

The 2,4-dinitrophenylhydrazone showed m.p. 195–198° (dark red needles from $CHCl_3$–MeOH); λ_{max} ($CHCl_3$) 410 mμ; ε, 31,600; IR bands at 3350 cm^{-1} (NH group), at 1738 cm^{-1} (Ac group), at 1615 and 1588 cm^{-1} (C=C double bonds). (Found: C, 58·96; H, 5·26; O, 23·84; N, 12·00. Calc. for $C_{23}H_{24}O_7N_4$: C, 58·97; H, 5·16; O, 23·81; N, 11·96%.)

Dihydrodecompostin (IIa). Decompostin (Ia; 1 g) in AcOEt (25 ml) was reduced over 5% Pd–C (100 mg) until the absorption of H_2 ceased. The soln was filtered and evaporated to dryness. Crystallization of the residue from ether–hexane afforded IIa (800 mg) as brilliant plates m.p. 148–152°. Further crystallizations from acetone–hexane raised the m.p. to 153–154°; $[\alpha]_D$ −70°; λ_{max}; 278 mμ; ε, 14,400; IR bands at 1740 cm^{-1} (Ac group), at 1677 cm^{-1} (dienone) and at 1610 cm^{-1} (furane double bonds). (Found: C, 70·81; H, 7·53; O, 22·12. Calc. for $C_{17}H_{22}O_4$: C, 70·32; H, 7·64; O, 22·04%.)

The 2,4-dinitrophenylhydrazone showed m.p. 230–231° (red plates from $CHCl_3$–MeOH); $[\alpha]_D$ −81°; λ_{max} ($CHCl_3$); 392 mμ; ε, 33,100; IR bands at 3280 cm^{-1} (NH group), at 1730 cm^{-1} (Ac group), at 1615 and 1590 cm^{-1} (C=C double bonds). (Found: C, 58·57; H, 5·53; O, 23·75; N, 11·94. Calc. for $C_{23}H_{26}O_7N_4$: C, 58·71; H, 5·57; O, 23·81; N, 11·94%.)

Desacetyldihydrodecompostin (IIb). A soln of IIa (200 mg) in MeOH (10 ml) was heated under reflux with KOH (200 mg) in water (1 ml) for 30 min. The solvent was removed *in vacuo*, water was added and the mixture was extracted with ether. The organic layer was washed with water, dried and evaporated to dryness. The residue was crystallized from ether–hexane yielding 40 mg of IIb, m.p. 158–159°. Further crystallizations from ether–hexane raised the m.p. to 162–163°; $[\alpha]_D$ ±0°; λ_{max}; 284 mμ; 20,800; IR bands at 3650 cm^{-1} (OH group), at 1665 cm^{-1} (dienone), at 1618 and 1540 cm^{-1} (furane double bonds). (Found: C, 72·95; H, 7·65; O, 19·13. Calc. for $C_{15}H_{20}O_3$: C, 72·55; H, 8·12; O, 19·33%.)

Acetylation of IIb with Ac_2O–pyridine furnished the acetate IIc, m.p. 112°; λ_{max}; 240, 284 mμ; ε, 3500, 12,500; IR bands at 1724 cm^{-1} (acetate), at 1670 cm^{-1} (dienone) and at 1610 cm^{-1} (furane double bonds). (Found: C, 70·18; H, 7·64; O, 22·29. Calc. for $C_{17}H_{22}O_4$: C, 70·32; H, 7·64; O, 22·04%.)

CrO_3 *oxidation of desacetyldihydrodecompostin* (IIb). A soln of IIb (70 mg) in pyridine (1 ml) was treated with CrO_3 (70 mg) in the same solvent (5 ml), left overnight at room temp, poured in cold water and extracted with ether. The organic soln was washed with dil HCl, $NaHCO_3$aq and water, dried and evaporated to dryness. The crude product (IVa) showed IR bands at 1675 cm^{-1} (α,β-unsaturated 6-membered ketones), at 1615 and 1520 cm^{-1} (furane double bonds). It was chromatographed on alumina. Elution with benzene gave oily residues which were combined and converted to the 2,4-dinitrophenylhydrazone (IVb). Crystallization from $CHCl_3$–MeOH yielded red plates m.p. 250–252°; λ_{max} ($CHCl_3$); 396 mμ; ε, 27,500; IR bands at 3630 cm^{-1} (NH group), at 1675 cm^{-1} (α,β-unsaturated 6-membered ketone), at 1615 and 1590 cm^{-1} (furane double bonds). (Found: C, 58·94; H, 5·37; O, 22·74; N, 12·86. Calc. for $C_{21}H_{22}O_6N_4$: C, 59·15; H, 5·20; O, 22·51; N, 13·14%.)

LAH *reduction of dihydrodecompostin* (IIa). A soln of IIa (500 mg) in THF (50 ml) was heated under reflux with LAH (500 mg) for 4 hr. AcOEt (10 ml) and sat Na_2SO_4aq (5 ml) were added. The soln was dried, filtered and evaporated to dryness. The residue (200 mg) showed m.p. 109–110°. Further recrystallizations from acetone–hexane raised the m.p. to 133–135·5°; $[\alpha]_D$ +52·7°; λ_{max}; 222 mμ; ε, 7700; IR bands at 3615 cm^{-1} (OH groups), at 1620 and 1545 cm^{-1} (furane double bonds). (Found: C, 72·38; H, 8·86; O, 19·07. Calc. for $C_{15}H_{22}O_3$: C, 71·97; H, 8·86; O, 19·17%.)

Tetrahydrodecompostin (III). Catalytic hydrogenation of IIa (250 mg) with PtO_2 (70 mg) in AcOEt gave 140 mg of III, m.p. 158–159° (plates from acetone–hexane), $[\alpha]_D$ −8°; λ_{max}; 278 mμ; ε, 260; IR bands at 1745 cm^{-1} (Ac group) and at 1720 cm^{-1} (cyclohexanone). (Found: C, 69·53; H, 8·29; O, 21·91. Calc. for $C_{17}H_{24}O_4$: C, 69·84; H, 8·27; O, 21·89%.)

2-*Bromodecompostin* (VI). A soln of Ia (300 mg) in CCl_4 (30 ml) was heated under reflux with NBS (200 mg) and benzoyl peroxide (5 mg) for 2 hr, washed with water, dried and evaporated to dryness *in vacuo*. The residue was crystallized from $CHCl_3$–ether yielding prisms (270 mg) m.p. 191–193° (dec); $[\alpha]_D$ −41·4°, λ_{max}; 250, 306 mμ; ε, 6000, 17,300; IR bands at 1740 cm^{-1} (acetate), at 1665 cm^{-1} (cross conjugated

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* Chromatography of the mother liquors led to the isolation of the previously described constituents of the hexane extract of *Cacalia decomposita*. In a recent collection of the roots we were unable to isolate decompostin.

6-membered ketone), at 1620 and 1598 cm^{-1} (C═C double bonds). (Found: C, 55·40; H, 5·24; O, 17·46; Br, 21·71. Calc. for $C_{17}H_{19}O_4Br$: C, 55·54; H, 5·44; O, 17·42; Br, 21·76%.)

2-*Ketodecompostin* (VII). A soln of VI (1·4 g) in t-BuOH (100 ml) was mixed with a soln of $AgNO_3$ (2 g) in water (10 ml) and heated under reflux for 15 min and the AgBr ppt was filtered off. The soln was diluted with water and extracted with ether. The ethereal extract was washed with water, dried and evaporated to dryness. The residue dissolved in benzene was chromatographed on alumina. Elution with benzene afforded VII (90 mg) m.p. 220–221° (prisms from acetone–hexane); $[\alpha]_D$ −31·5°; λ_{max}; 258 and 320 mμ; ε, 6600, 9300; IR bands at 1740 cm^{-1} (Ac group), at 1668 (α,β-unsaturated 6-membered ketones) and at 1600 cm^{-1} (C═C double bonds). (Found: C, 67·41; H, 6·24; O, 26·00. Calc. for $C_{17}H_{18}O_5$: C, 67·54; H, 6·00; O, 26·46%.)

Treatment of decompostin (I) *with acetic anhydride and* H_3PO_4. A soln of Ia (80 mg) in Ac_2O (5 ml) and 85% H_3PO_4 (1 ml) was heated on the steam bath for 1 hr, water was added and the ppt was extracted with AcOEt. The organic layer was washed with water, $NaHCO_3$ aq, dried and evaporated to dryness. The fluorescent residue was chromatographed on alumina (2 g). Elution with hexane gave some crystalline fractions. They were combined and recrystallized from ether–pentane yielding pale yellow prisms (15 mg) m.p. 105–106°; λ_{max} 216, 253, 260 and 329 mμ; ε, 16,200, 12,000, 11,700, 26,300; IR bands at 1778 cm^{-1} (phenolic acetate), 1668 cm^{-1} (α,β-unsaturated ketone) and at 1615 cm^{-1} (C═C double bonds). (Found: C, 72·65; H, 6·35; O, 20·68. Calc. for $C_{19}H_{20}O_4$: C, 73·06; H, 6·45; O, 20·49%.)

Acetyl bisdehydrocacalol acetate (IX). Bisdehydrocacalol acetate (X^2; 100 mg) was treated in the same manner as described in the above preparation. Crystallization from ether–hexane yielded yellow needles (60 mg) m.p. 165–167°; λ_{max}; 228, 269, 326 (shoulder) and 341 mμ; ε, 33,500, 37,200, 13,400, 18,000; IR bands at 1775 cm^{-1} (phenolic acetate), 1680 cm^{-1} (α,β-unsaturated ketone), at 1650 and 1575 cm^{-1} (C═C double bonds); NMR singlets at 2·50, 2·59, 2·79, 2·84 and 3·00 (acetyl, acetate, furane and aromatic Me groups) signals at 7·2, 7·36 and 7·78 (3H, aromatic protons). (Found: C, 73·70; H, 5·82; O, 20·43. Calc. for $C_{19}H_{18}O_4$: C, 73·53; H, 5·85; O, 20·62%.)

Zn-*pyridine reduction of decompostin* (Ia). A soln of Ia (500 mg) in pyridine (20 ml) and water (0·2 ml) was treated with activated Zn dust[12] (5 g), heated under reflux with mechanical stirring for 2 hr. The soln was filtered, diluted with water and extracted with ether. The ethereal extract was washed with dil HCl, water, dried and evaporated to dryness. The residue was chromatographed on alumina. Elution with benzene–ether (9:1) gave 20 mg of partially crystalline material. Elution with more polar solvents gave intractable gums. The partially crystalline material showed IR bands at 1675 cm^{-1} (ketone conjugated with the furane ring) and at 1600 cm^{-1} (C═C double bonds). Its NMR spectrum (in CCl_4) showed a singlet at 0·78, a doublet at 0·92 (J = 7 c/s) and a doublet at 1·98 (J = 1 c/s) corresponding to the C-5, C-4 and C-11 Me groups, respectively. The C-6 allylic protons are responsible for a pair of doublets (J = 16 c/s) centered at 2·72 and 2·30. The latter partially superimposed on other signals. A quadruplet (J = 1 c/s) at 7·30 is ascribed to the furane proton. This NMR spectrum was identical to that shown by an authentic sample of furanoeremophylone (XI).

The 2,4-dinitrophenylhydrazone had m.p. 286–290° (orange needles from $CHCl_3$–MeOH). (Found: C, 61·09; H, 5·92; O, 19·58; N, 13·31. Calc. for $C_{21}H_{24}O_5N_4$: C, 61·15; H, 5·87; O, 19·40; N, 13·59%.) Mixed m.p. with the 2,4-dinitrophenylhydrazone of furanoeremophylone (m.p. 289–293°) were undepressed and the IR spectra were identical.

REFERENCES

[1] Contribution No. 245 from the Instituto de Química de la Universidad Nacional Autónoma de México.
[2] J. Romo and P. Joseph-Nathan, *Tetrahedron* **20**, 2331 (1964).
[3] P. Joseph-Nathan, J. J. Morales and J. Romo, *Tetrahedron* **22**, 301 (1966).
[4] J. Correa and J. Romo, *Tetrahedron* **22**, 685 (1966).
[5] H. Ishii, T. Tozyo and H. Minato, *Tetrahedron* **21**, 2605 (1965).
[6] N. P. Buu Hoi, N. D. Xuong and N. V. Bach, *J. Chem. Soc.* 173 (1964).
[7] L. Novotný, V. Herout and F. Šorm, *Tetrahedron Letters* No. 20, 697 (1961).
[8] L. Novotný, J. Jizba, V. Herout and F. Šorm, *Coll. Czech. Commun.* **27**, 1393 (1962).
[9] L. Novotný, V. Herout and F. Šorm, *Coll. Czech Commun.* **27**, 1401 (1962).
[10] [a] K. Tsuda, E. Ohki and S. Nozoe, *J. Org. Chem.* **28**, 783 (1963), **28**, 786 (1963).
[b] K. Tsuda, S. Nozoe and Y. Okada, *Ibid.* **28**, 789 (1963).
[c] S. M. Sharif, S. Nozoe, K. Tsuda and N. Ikekawa, *Ibid.* **28**, 793 (1963).
[11] L. Novotný, J. Jizba, V. Herout, F. Šorm, L. H. Zalkow, S. Hy and C. Djerassi, *Tetrahedron* **19**, 1101 (1963).